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CHEMICAL AND PHYSICAL ANALYSIS OF LAMINATED SEDIMENT FORMED IN LOE POOL, CORNWALL

Pickering, David Alan

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CHEMICAL AND PHYSICAL ANALYSIS OF

LAMINATED SEDIMENT FORMED IN LOE

POOL, CORNWALL.

by David Alan Pickering B.Sc.

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Department of Environmental Sciences,

Faculty of Science,

Plymouth Polytechnic,

Plymouth,

Devon.

In collaboration with:

Institute for Marine Environmental Research,

Prospect Place,

The Hoe,

Plymouth.

Abstract

Chemical and Physical Analysis of Laminated Sediment Formed in Loe Pool, Cornwall.

David Alan Pickering   March 1987

Laminated and annually-laminated sediments are found in Loe Pool. The origins of such laminations are investigated and evidence for their conditions of formation are presented.

In all sediment analysed the combustion residue was greater than 80%, and in the black and grey annually-laminated sediment the organic matter was less than 3%. This indicated that the sediment was dominated by a minerogenic input. The high lacustrine sediment concentrations of copper, zinc and other heavy metals together with evidence from analysis of magnetic variables which indicated high levels of haematite, confirmed that a major sediment source was effluent from mine waste.

Analysis of individual black and grey annual laminations revealed increased concentrations of chlorophyll $\underline{c}$, phaeopigments and perylene together with a lower C:N ratio in the black lamination. This indicated formation of the black layer in the summer months. From the high iron:manganese ratio and the low concentrations of calcium and carbonate in the black lamination as compared with the grey layer it was apparent that the black lamination was formed under conditions of oxygen shortage, and the grey lamination was formed when the bottom waters were fully oxygenated. It was concluded that from the analysis of selected physical and chemical properties of individual laminations it was possible to identify the principal sediment source, the likely season of deposition of each lamination and the palaeo-redox condition of the lake at that time.

From this information a hypothesis of the formation of the laminated sediments in Loe Pool is proposed. It is suggested that a dominant factor controlling sediment composition was the redox conditions at the time of deposition. These conditions were primarily influenced by lake depth, lake mixing, input of allochthonous material and the oxygen demand of sedimenting material.

This thesis is submitted for the degree of Doctor of Philosophy of Plymouth Polytechnic through the Council of National Academic Awards. It has not been submitted in any part for another degree. The described work, except for the portions for which due acknowledgement is made in the text, is my own work.

David A. Pickering

I dedicate this thesis to my wife Jan and
my parents Roger and Jean with thanks for
all their help and encouragement.

HEAVEN

Fish (fly-replete, in depth of June,

Dawdling away their wat'ry noon)

Ponder deep wisdom, dark or clear,

Each secret fishy hope or fear.

Fish say, they have their Stream and Pond;

But is there anything Beyond?

This life cannot be All, they swear,

For how unpleasant, if it were!

One may not doubt that, somehow, Good

Shall come of water and of Mud;

And, sure, the reverent eye must see

A Purpose in Liquidity.

We darkly know, by faith we cry,

The future is not Wholly Dry.

Mud unto mud!-Death eddies near-

Not here the appointed End, not here!

But somehow, beyond Space and Time,

Is wetter water, slimier slime!

And there (they trust) there swimmeth One

Who swam ere rivers were begun,

Immense, of fishy form and mind,

Squamous, omnipotent, and kind;

And under that Almighty Fin,

The littlest fish may enter in.

Oh! never fly conceals a hook,

Fish say, in the Eternal Brook,

But more than mundane weeds are there,

And mud, celestially fair;

Fat caterpillars drift around,

And Paradisal grubs are found;

Unfading moths, immortal flies,

And the worm that never dies.

And in that Heaven of all their wish,

There shall be no more land, say fish,

Rupert Brooke, 1913.

Acknowledgements

variables.

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List of Abbreviations

bp	before present
c.	_circa_
C. of V.	coefficient of variation
Chl	chlorophyll
C-G.C.-M.S.	Computerised-Gas Chromatography-Mass Spectrometry
C.P.I.	Carbon preference index
D.W.	Dry weight
G.C.	Gas Chromatography
H.P.L.C.	High Pressure Liquid Chromatography
lam	lamination
L.O.I.	Loss on ignition
L.P.	Frozen core collected from Loe Pool
M	Mackereth Core collected from Loe Pool
O.D.	Ordnance Datum
S.I.R.M.	Saturated Isothermal Remanent Magnetism.

Glossary

allochthonous   derived from the catchment area supplying the lake

autochthonous   produced within the lake body

epilimnion   the relatively warm upper layer of a stratified lake

eutrophic   a lake enriched in nutrients

hypolimnion   the relatively cold layer at the bottom of a stratified lake

oligotrophic   a lake poor in nutrients

overturn   mixing of the epilimnion and hypolimnion

CHAPTER 1 Introduction to the Study of Laminated Sediments

1.1 Introduction to Research at Loe Pool

Loe Pool (Fig. 1) is a shallow eutrophic freshwater lake (latitude 50" 4' N, longitude 5" 17' W) at approximately 4m O.D., 1 Km south of Helston, Cornwall, UK, (G.R. S.W. 648 250). The Pool, which has an area of 55.6 ha, was probably formed in medieval times by the damming of the River Cober with a shingle bar (Coard et al., 1983). Loe Pool and most of the land immediately surrounding the lake are owned by the National Trust. Some rights are retained by the Rogers family to whom the estate originally belonged. Studies of the Loe Pool catchment were initiated from Plymouth Polytechnic in the late 1970's to investigate the occurrence of algal blooms.

In order to investigate the history of the lake, attention was focussed on an examination of both, the sediment stratigraphy for various properties, and of documents that detailed past events in the catchment (Coard, in prep.). Subsequent limnological studies were formulated to study the population of algae (Greaves, in prep.) and the nutrient status of the lake (Lacey, in prep). The aim of the work was to produce a plan for managing the Loe Pool system. Investigation of the sediment stratigraphy revealed laminated clays including a series of annual laminations (Simola, Coard & O'Sullivan, 1981). From the surface sediment there is a series of brown/dark brown clays, pink haematite rich/grey clays,
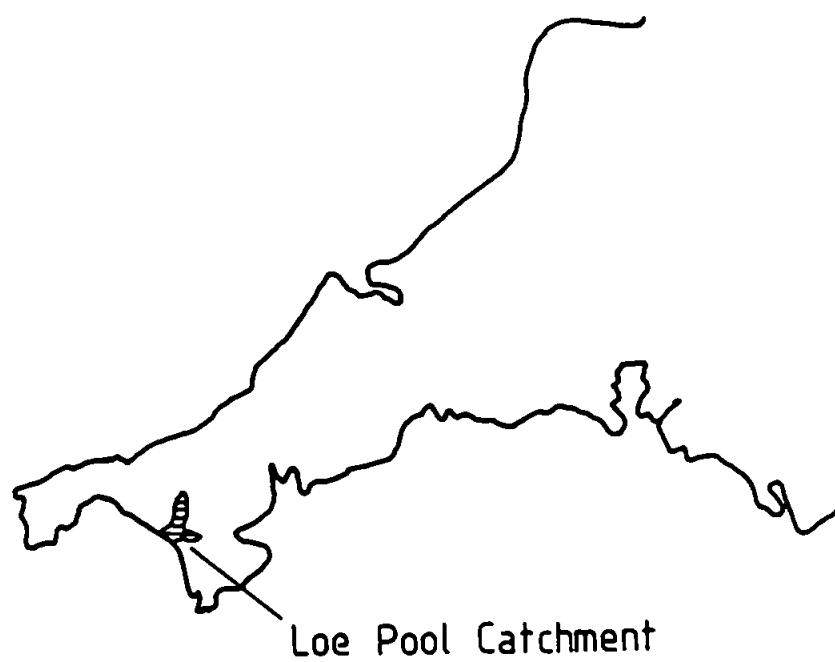
Figure 1. Location map of Loe Pool in South West England.

regularly laminated black/grey clays, and brown clay with fine laminations (Fig. 2) (O'Sullivan et al., 1984). Selected laminations from the surface brown/dark brown clay and the black/grey sediment sequence were identified to be annually-formed (Simola et al., 1981). The authors examined the sediment and found repeated cycles of diatoms, these were attributed to seasonal algal production and sedimentation.

In the top brown sediment (0-5 cm) the lighter coloured laminations were reported to be formed in the summer and the darker in the winter. Conversely, in the black/grey sediment unit (120-300 cm), the black laminations were formed in the summer and the grey in the winter (Simola et al., 1981).

Simola et al. (1981) suggested that the presence of annually-laminated sediment may reflect either:

1) regular changes within the lake ecosystem

or 2) variation in the intensity of erosion and transport of material from the catchment, particularly where instability in the lake-watershed has occurred as a result of human activities.

It is possible that the laminated sediment formed in Loe Pool may have resulted from a combination of these factors.

Lacustrine sediment has two principal sources, the allochthonous fraction supplied from the catchment and the autochthonous material which is produced within the lake. At Loe Pool both the autochthonous and allochthonous fraction are influenced by seasonal variations. The terrestrial sediment load increases in the winter months as a response to increased rainfall and streamflow (section 2.1) and the autochthonous input maximises

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Figure 2. Sediment stratigraphy of the deepest core sampled from Loe Pool (from O'Sullivan et al., 1984).

in the summer months when aquatic production peaks (section 2.2).

The limnological conditions within Loe Pool also change on a seasonal basis and hence may influence the formation of the laminated sediment. At present the lake is well mixed and oxygenated throughout the winter. In contrast during the summer months there are periods of oxygen stress and anoxia at the sediment-water interface (Greaves pers. comm., section 2.2.2). In times when these black/grey laminations were being formed (1920's and before) the lake would have been deeper and conditions potentially even more conducive for summer anoxia at the sediment-water interface (O'Sullivan et al., 1984).

Each of the sediment sequences reported from Loe Pool contained individual laminations at least 1 cm thick. The sediment is, therefore, of great interest to palaeolimnologists, because it offers both the chance to further study the history of Loe Pool, and also to investigate chemical and physical properties of individual laminations, which may be used as markers of a seasonal input in other lakes.

This thesis reports on selected chemical and physical properties of the laminated sediment of Loe Pool, Cornwall. It is part of a wider investigation of Loe Pool and its catchment. Other workers have produced or are preparing reports on:

1) Annual laminations in the sediments of Loe Pool, Cornwall (Simola et al., 1981).

2) The use of laminated lake sediments in the estimation and calibration of erosion rates (O'Sullivan, Coard & Pickering,

1982).

3) Paleolimnological studies of annually-laminated sediments in Loe Pool, Cornwall, U.K. (Coard et al., 1983).

4) Studies of the formation and deposition of annually-laminated sediments in Loe Pool, Cornwall, U.K. (O'Sullivan et al., 1984).

5) The use of X-ray fluorescence spectrometry in paleolimnology (Cousen & O'Sullivan, 1984).

6) Paleolimnological study of the history of Loe Pool, Helston, and its catchment (Coard, Ph.D. thesis in prep.).

7) A study of the nutrient budget of the Loe Pool catchment, Cornwall, England.(Lacey, Ph.D. thesis in prep.).

8) An investigation into the ecology of phytoplankton in Loe Pool, Cornwall. (Greaves, Ph.D thesis in prep.).

In addition, there are several unpublished undergraduate projects on aspects of the Loe Pool Catchment.

1.2 Classification of Lacustrine Systems

Lakes are widely studied geomorphological features (Hutchinson,

1957; Hutchinson, 1967; Hutchinson, 1975; Cole, 1983; Wetzel, 1983). They may be described according to a variety of features including morphometry, nutrient status, limnological characteristics and climatic influence. Examples of these are summarised in Table 1.

1.3 Sediment Formation

The sediment that forms beneath a lake is the function of (a) inputs to the lake, (b) processes within the aquatic system, (c) deposition of matter to the sediment and (d) post sedimentation diagenesis (Fig. 3). Any palaeolimnological investigation should, therefore, consider all relevant factors when interpreting results.

1.4 Lake Watershed-Ecosystem Concept

Within science, prediction and monitoring of environmental changes have often been based on both large and small scale empirical models. For example, the global modelling of the climate following a nuclear war (Thompson et al., 1984) or the measurement of stream flow and its relationship to precipitation (Singh, 1982). Frequently both of these approaches have shortcomings because of their limitations in both space and time. One attempt at overcoming these restrictions is the systems approach.

Oldfield (1977) notes that conceptual frameworks based on systems-thinking have become more important in recent years. One

Classification	Description
Morphometry:	
Deep	
Shallow	
Nutrient Status:	
Eutrophic	Productive
Oligotrophic	Low Productivity
Limnological:	
Meromictic	Permanently Stratified
Dimictic	Two Seasons of Mixed Water
	Two Seasons with Stratification
Monomictic	One Season of Stratification
Climatic Influence:	
Temperate	
Tropical	
Geographical:	
Inland	
Coastal	
Low Altitude	
High Altitude	

Table 1. Examples of Lake Classification.

Terrestrial
system   Atmosphere

                                         precipitation   evaporation
                                         particulate
          run-off   fallout

                              ┌──────────────────────────────┐
                              │ Processes   │
                              │   │
Lake   │ e.g. production   │
system   │   oxidation   │
                              │   reduction   │
                              │   biological decay   │
                              └──────────────────────────────┘

                     sedimentation   resuspension
                                                dissolution
                                                gaseous emission

                              ┌──────────────────────────────┐
                              │ Early diagenetic processes   │
                              │   │
                              │ e.g.   microbial activity   │
Sediment   │   chemical activity   │
                              │   physical compression   │
                              └──────────────────────────────┘
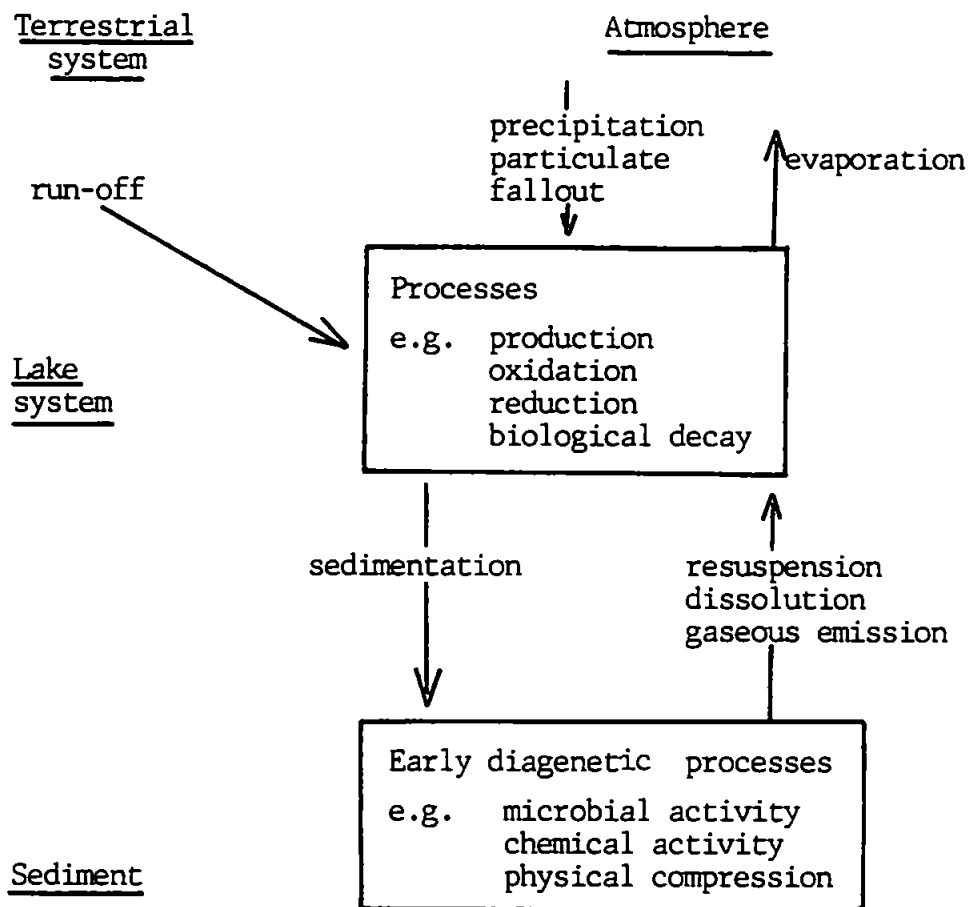
Figure 3   Factors influencing sediment formation.

example is the Ecosystem-Watershed concept (O'Sullivan, 1979). This concept subjugates spatial limitations by using the catchment as the basic land area. This approach originated with the Hubbard Brook Watershed-Ecosystem Study (Bormann & Likens, 1969) and is summarised in Figure 4. The model has been extended to include a time perspective by the inclusion of information from lake sediment (Likens & Bormann, 1975).The lake watershed-ecosystem concept has been presented in diagrammatic form by O'Sullivan (1979), (Fig. 5). The sediment which accumulates in lakes can be likened to a data storage bank holding records of past conditions and events within the water body and drainage basin. The work of palaeolimnologists within such an approach is to "translate into a readable form " the information stored in this data base.

1.5 Introduction to Palaeolimnology

Palaeolimnologists aim to characterise selected properties of lake sediment in order to understand the development of the lake and its drainage basin. This is achieved by the use of techniques from many disciplines. These may be separated into three broad subject areas of biological, physical and chemical analyses. Some of the most widely investigated properties of lake sediment together with examples of their applications are shown in Table 2.

Palaeolimnologists have studied lake sediments in order to investigate changes over many time scales. For example, analyses of pollen content and chemical and physical properties of dated sediment cores from the English Lakes have shown changes in

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┌─────────────────────────────┐
│ CULTURAL SYSTEMS            │
│ Agriculture, Forestry, Mining│
│ Settlement, Urbanisation,   │
│ Industrialisation.          │
└─────────────────────────────┘

┌─────────────────────────────┐
│ ECOSYSTEM-WATERSHED         │
│ Changes promoted by changes │
│ in cultural components of system.│
└─────────────────────────────┘

┌─────────────────────────────┐
│ OUTPUT CHANGES              │
│ Increased run-off and sediment│
│ yield, changes in biological│
│ productivity, landform changes.│
└─────────────────────────────┘
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Feedback

Feedback
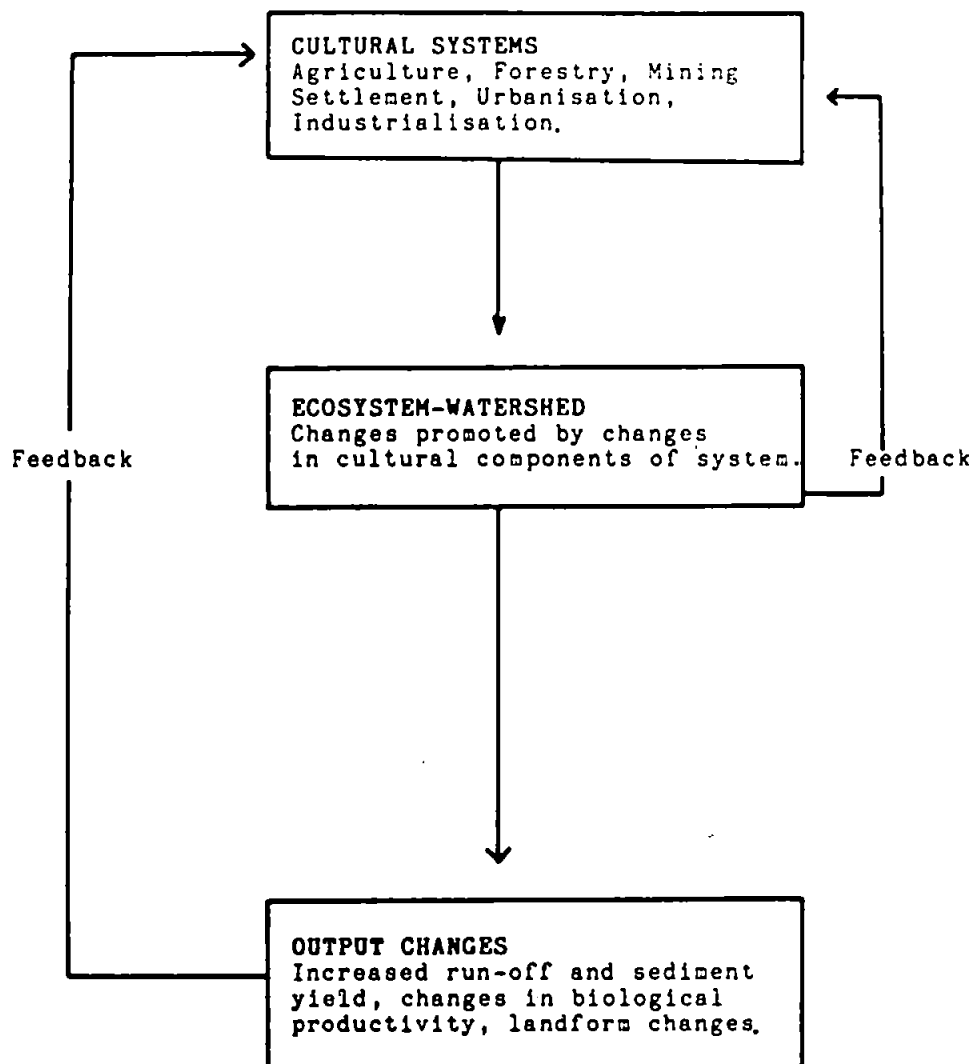
Figure 4. Relationship between cultural systems
and ecosystem-watersheds (from O'Sullivan, 1979).

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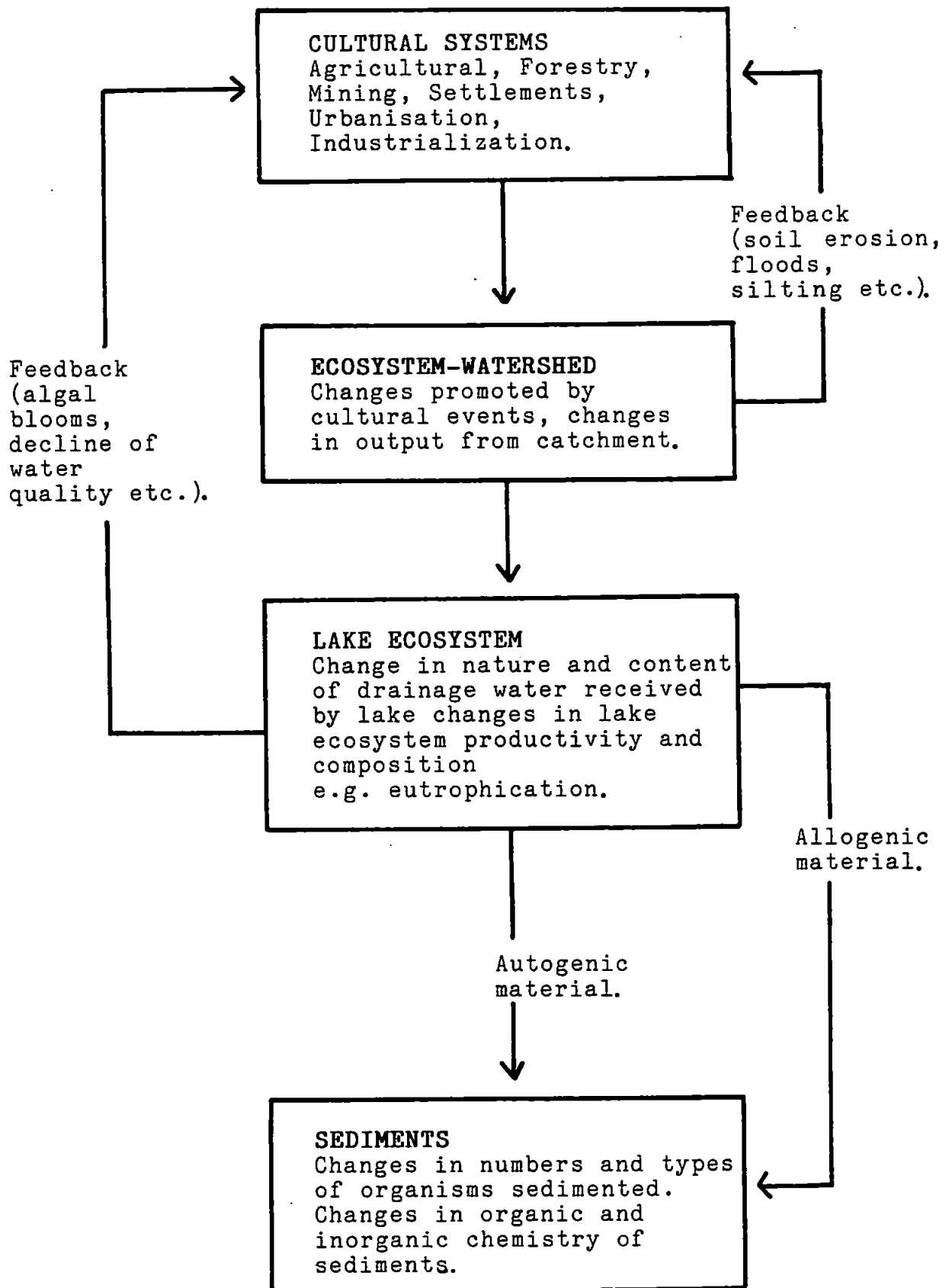
Figure 5. Relationship between cultural systems and sediments in ecosystem-watersheds (from O'Sullivan, 1979).

Table 2. Selected Applications of Lake Sediment Properties.

	Property	Application	References
Biological	Diatoms	Trophic Status, Seasonality	Jorgensen, 1948; Simola, 1977
	Pollen	Identification of Annual-laminations	Tippett, 1964
	Cladoceran	Lake Ecology	Frey, 1976, 1979
Physical	Dry weight, Loss on ignition and Combustion Ratio	Indicate Proportion of Organic:Minerogenic Matter	Renberg, 1978a; Renberg and Segerström, 1981
	Magnetic Susceptibility/ S.I.R.M.	Sedimentation Patterns	Bloemendal and Oldfield, 1978
	S Ratio	Changes in Land Use	Björck, Dearing and Jonsson, 1982
	Natural Remanent Magnetism	Palaeomagnetic Sediment Dating	Thompson and Oldfield, 1978
	^{14}C, ^{137}Cs, ^{210}Pb	Radio Isotope Dating	Appleby and Oldfield, 1978; Pennington et al., 1976
Chemical	Pigments	Trophic Status	Gorham and Sanger, 1976
	Elements	Pollution, Redox Conditions	Heit et al., 1981; Mackereth, 1966
	Extractable Lipids	Trophic Status, Redox Conditions	Cranwell, 1977a, 1978; Didyk et al., 1978
	Carbonate	Seasonality of Input from Catchment Redox Conditions of Hypolimnion	Hilton and Gibbs, 1984/85

climate and vegetation from the late glacial to the present day (Pennington, 1981). In the Norfolk Broads palaeolimnologists have shown the process of cultural eutrophication over the past 100 years (Moss, Forrest & Phillips, 1979).

The potential for studies on even shorter time scales is limited by the ability to date sediment accurately. However, where annually-laminated sediments exist, individual years or even seasons can be examined.

1.6 Annually-Laminated Sediments

Investigation of some freshwater sediments have shown the existence of laminations (Nipkow, 1920; Ludlam, 1976; Renberg, 1976). Where more than one stratigraphic unit is deposited in a year, then the sediment is said to be seasonally-laminated. An annual lamination or varve is the sum of these individual layers which make up the sediment deposited in one year (O'Sullivan, 1983).

Annually-laminated sediments have distinct stratigraphic units, the content of which changes rhythmically. These may be formed by one or more variations in (a) the supply of allochthonous material (Sturm, 1979), (b) the deposition of autochthonous material (Huttunen & Tolonen, 1977), or (c) lake processes (Renberg, 1981a). Annual laminations can provide an absolute time scale for palaeolimnology and consequently have had many applications. These have been extensively reviewed (O'Sullivan, 1983) and include geochronological investigations of sediment sequences varying in

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time scales from thousands of years, for example, the measurement of the Hoxnian interglacial period (Turner, 1970), to decades; for example, the eutrophication of Zürichsee (Züllig, 1981). In addition such sediment has been used to calibrate other dating techniques, for example 210-Pb and 14-C (Appleby et al., 1979; Tolonen, 1980).

The use of improved coring techniques (Shapiro, 1958; Swain, 1973; Huttunen and Meriläinen, 1978) has enabled the retrieval of relatively undisturbed sediment stratigraphies. As a result, the number of lakes known to contain varved sediment has increased. They occur in North America, Central and Northern Europe, East Africa, Japan, Australia, Turkey and Central America (O'Sullivan, 1983).

Annual laminations may have different origins. O'Sullivan (1983) has reviewed the classification of laminations, and describes the following types :

calcareous - which form in lakes where there is a seasonal
            deposition of carbonate

ferrogenic - which form in iron-humic lakes where there is
            a seasonal change in redox conditions at the
            the sediment-water interface

clastic - which are composed principally of allochthonous
          material which may vary in size

and biogenic - which are produced by biological rather than
               chemical factors.

The identification of annual laminations, as distinct from laminae, caused by anomalous conditions or irregular changes in catchment use, is achieved by two main techniques:

1)   by counting a number of annual laminations down a core

and correlating the results with a dated section of

sediment,

and/or

2)   by studying individual laminations for specific

seasonal markers.

Using the first technique, dates have been obtained by historical evidence (Digerfeldt, Battarbee & Bengtsson, 1975; Saarnisto, Huttunen & Tolonen, 1977; Coard et al., 1983) and in longer sediment sequences from Carbon 14 data (Stuiver, 1971). However, these methods require long and uninterrupted sediment sequences and even in lakes where these exist, correlation between the number of annual laminations and the radiocarbon date has often been poor (Olsson, 1974; Tolonen, 1980).

By using the second technique, where the characteristics of individual laminations within a sediment sequence are studied, workers have found seasonal deposition of microfossils. Biological remains examined include diatoms (Simola, 1977), pollen grains (Tippett, 1964) and chrysophycean scales (Battarbee, 1981). The technique of studying diatom skeletal remains has been applied to the laminated sediment of Loe Pool, Cornwall (Simola et al., 1981) where it was verified that sequences of annual laminations are present.

Varved sediments have been studied at many sites. Saarnisto (1979) reported that the normal thickness of annual laminations in small undisturbed lakes is between 0.5 mm and 1.0 mm. This has precluded analysis of certain chemical and physical properties where large quantities of material (c. 1g) are required for quantitative

analysis. At Loe Pool, sediment has accumulated at an average rate of 3 cm per year for the past 110 years (Simola et al., 1981). Thus the varved sediment of Loe Pool affords a unique opportunity for detailed investigation of selected chemical and physical characteristics of individual seasonal laminations.

1.7 Aims of this Study

By the investigation of selected chemical and physical properties of individual laminations this study aimed to assess:

1) The likely source/sources of the sediment deposited in each lamination.

2) The likely season of deposition of each lamination.

3) The likely limnological conditions of the lake at the time of deposition of each lamination.

And hence to :

4) Develop a working hypothesis to explain the formation of laminated sediments in Loe Pool.

In addition :

5) This study aimed to highlight those chemical and physical

properties which have the greatest potential for revealing information in palaeolimnological investigations of laminated sediment.

1.8 Rationale of Thesis

Swain (1985) concludes that " Paleolimnology reveals cause and effect best when a number of parameters (e.g. geochemistry, absolute dating, and fossils such as diatoms, cladocerans and pollen) are examined together. As each stratigraphic parameter is added, the number of hypotheses that can account for the data is reduced until the history of a lake can be reconstructed with reasonable certainty" (p.73). To gain the most information in this study several chemical and physical properties of the individual seasonal laminations were analysed. In order to achieve the aims, properties were selected that might best show an aquatic or terrestrial bias in source, or differences in season of deposition, or variations with the seasonal redox conditions.

This thesis will initially present information from the catchment and lake of relevance to sediment formation, and describe stratigraphic sequences cored from Loe Pool prior to this study. The results of selected chemical and physical analyses of lake sediment reported in the literature will be reviewed. The potential application of each technique for the investigation of seasonally-deposited laminations is discussed.

Chapter 2   Site Description

2.1 Loe Pool Catchment

The Loe Pool catchment is located on the north-west edge of the Lizard Peninsula in south-west Cornwall (Fig. 1). The catchment has a total area of 55 square kilometres (Coard, in prep.). The geology, quaternary geology, climate, drainage system, land use of the catchment and limnology of the Loe Pool have been extensively reviewed, and sediment accumulation, researched by Coard (in prep.). This introduction to the catchment describes some of the factors that have influenced sediment formation in Loe Pool. Much of the information presented has been summarised from Coard (in prep.).

2.1.1 Geology

A geological map of the catchment drawn by Cousen (1981) is illustrated (Fig. 6). There are 3 main rock types, the Carnmenellis granite to the north , the Mylor beds to the west and Gramscatho beds to the east.

The Carnmenellis granite is one of a series of granite bosses intruding in a west-south-west line from Dartmoor to the Scilly Isles. The intrusion occurred between the Upper Carboniferous and Permian periods, approximately 275 million years ago (Barton, 1964).
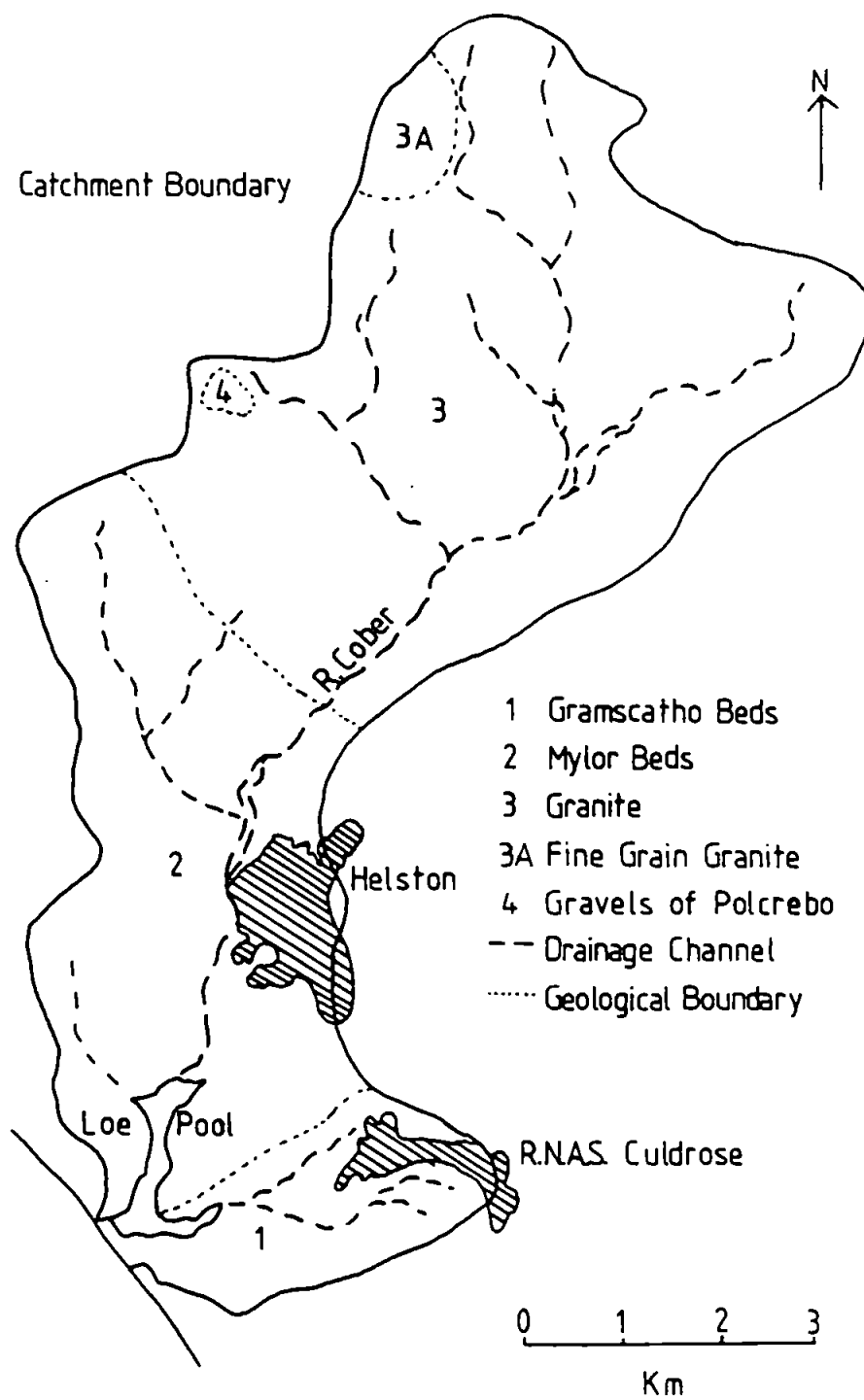
Figure 6. Geology of the Loe Pool catchment
(from Cousen, 1981).

The legend of the figure reads:

1 Gramscatho Beds
2 Mylor Beds
3 Granite
3A Fine Grain Granite
4 Gravels of Polcrebo
— — Drainage Channel
········ Geological Boundary

Catchment Boundary

Helston

Loe Pool

R.N.A.S. Culdrose

R. Cober

Around the Carnmenellis granite is an area of highly mineralised contact-metamorphism intruding into the Mylor slate beds for 1-2 Km. (Flett & Hill, 1946).

The Mylor beds to the west of Loe Pool are dark shales with thin bands of pale, sandy sediment. The rocks are intensively folded and may be permeated by veins which are generally highly crystalline quartz but which may include shales, chlorites, carbonates, iron oxides and pyrites (Flett & Hill, 1946). These slates contain more alumina, magnesium and iron oxides and less silica and alkaline elements than the granite. The Gramscatho beds to the east of Loe Pool are a group of grits and shales with occasional limestones (Edmunds, Mckeown & Williams, 1975).

Throughout the Quaternary period the catchment was subjected to periglacial conditions and sea level fluctuations. Coard (in prep.) and references therein cite evidence of raised beaches, head and alluvial deposits. The head deposits are found on both sides of Loe Bar and consist of local slates and quartz. In the Cober valley there are considerable depths (approx. 10m) of coarse-grained material from the granitic intrusion and the surrounding metamorphic aureole. This material was subsequently overlain by peat deposits. Some marine clays were also deposited in the valley during the Pleistocene Age when the sea level was higher.

2.1.2. Loe Bar

Loe Pool is separated from the sea by a shingle bar. This was thought to have been formed by the process of longshore drift (Toy, 1934). The time of bar formation is not accurately known (Coard, in

prep.), but in 1546 the bar was described as an almost permanent feature. Presumably around this period, the water changed from estuarine to freshwater.

Evidence (Coard, in prep. and references therein) suggest that Loe Bar is a developing feature. The bar is now of a sufficient size that the lake would only receive inwash of seawater in the most severe storms. In the 16th, 17th, and 18th centuries, before the bar was so large a structure, water would percolate through it to the sea. Because the rate of percolation was sometimes less than the input of river water to Loe Pool, the lake level would rise. Periodically this rise would cause flooding in the lower areas of Helston. When this occurred the bar was broken, by the cutting of a channel, in order to release the water.

To prevent regular flooding an "adit" was opened in the late 18th century to allow discharge of water to the sea. This was often blocked after storms and to reduce the frequency of this the "adit" was enlarged in 1899. The provision of this channel has stabilised the lake level throughout the 20th century, although the bar has been broken to alleviate flooding following obstruction of the outflow. Bar breaking occurred on an almost annual basis through the later half of the 19th and early part of the 20th century (Coard, in prep.).

Because of the bar's growth and particularly the deposition of impervious clays from mine waste, it is unlikely that there will be a large amount of seepage at the present time. According to Coard (in prep.), a 1967 Cornwall River Authority report recorded no significant movement of water in either direction. These factors may explain why Loe Pool has no brackish influence despite the

lakes's proximity to the sea.

2.1.3 Catchment Drainage

The catchment is drained by three main streams, of which the largest is the River Cober (Fig. 7). The watershed of the Cober is to the north of the pool and covers approximately 73% of the Loe Pool catchment, including land previously worked for tin. The Penrose and Carminowe Streams drain the west and east side of the catchment respectively.

2.1.4 Climate

The Lizard Peninsula has a temperate maritime climate with prevailing winds from the south-west. Seasonal average temperatures vary between $5^{\circ}C$ in February to $16^{\circ}C$ in August (Fig. 8).

Rainfall also varies seasonally, with maximum levels in the months of October to February and minimum from April to August (Fig. 8). With more evapotranspiration in the summer months, the seasonality of the streamflow is even more marked than the rainfall (Fig. 8). The streamflow of the River Cober is lowest from May to October and highest from December to March. Approximately 3.7 times as much water flows in the Cober in the 6 months from November to April than in the 6 months May to October. The erosive and transporting capacity of the stream is consequently greater in the winter than summer months, so there is a marked seasonality in both water flow and material transported to Loe Pool.

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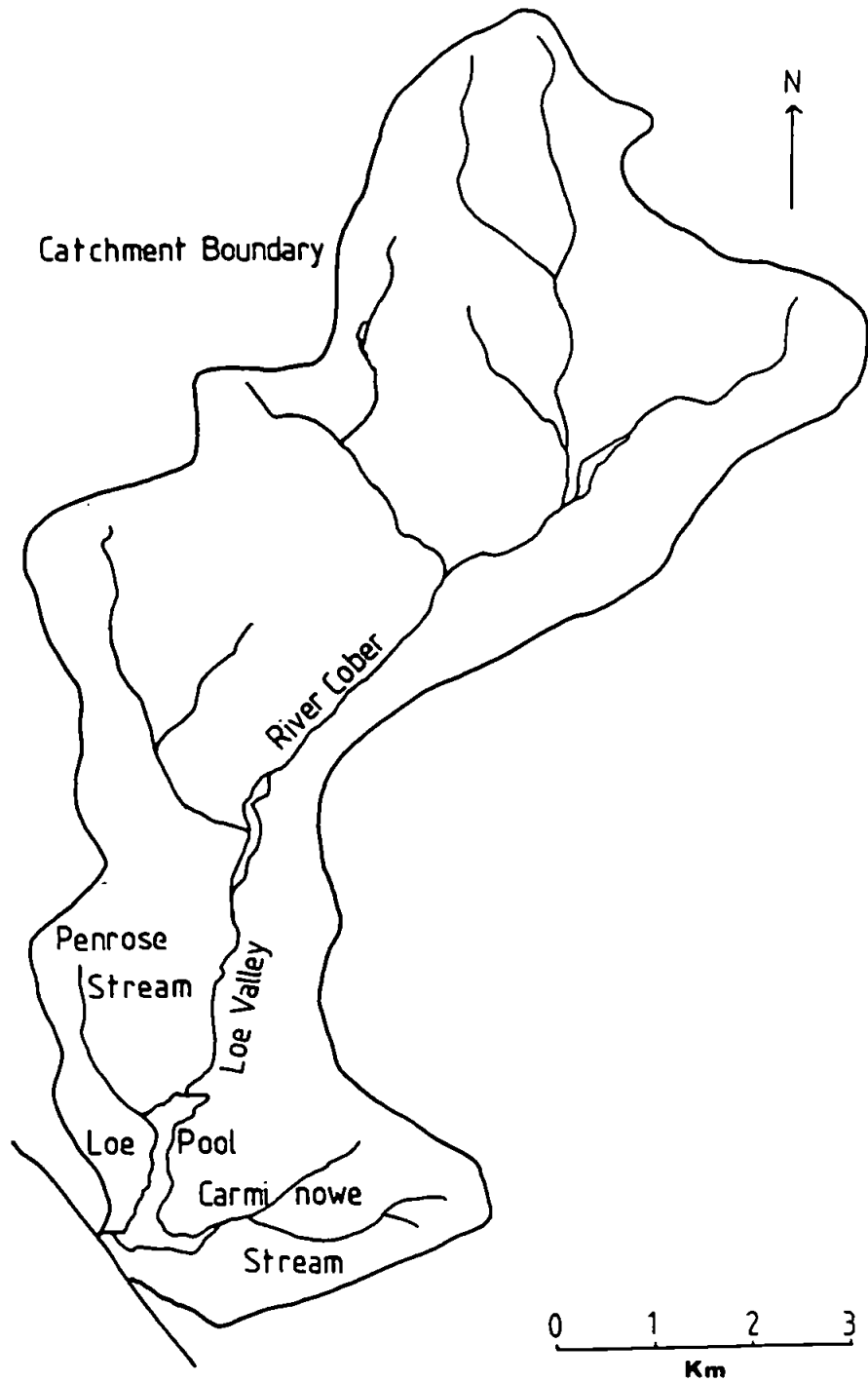
Figure 7. Drainage of the Loe Pool Catchment
(from Cousen, 1981).
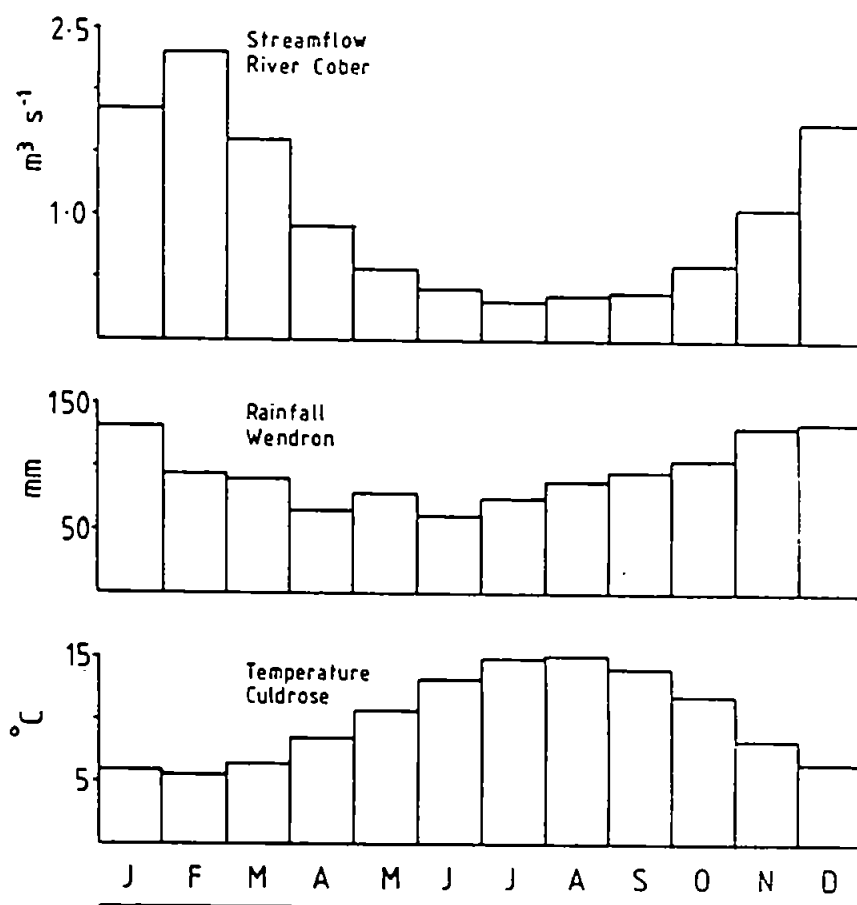
Figure 8. Mean monthly stream-flow (River Cober 1970-1979),
mean monthly rainfall (1941-1970) and mean monthly
temperature (1960-1974) for the Loe Pool catchment.
(from Simola et al., 1981).

2.1.5 Land Use

No land use map of the catchment is currently available. However Coard (in prep.) notes that over 40% of the catchment is moorland with thin acid soils. The remainder is largely agricultural, varying in use from permanent pasture on higher ground to arable and market gardening in the south of the catchment. Some of the areas which have been worked for tin are now largely wasteland which is reverting to acid heathland or scrub.

Although mining no longer occurs within the Loe Pool catchment, previous operations have had a significant effect upon the Pool and the sediment accumulation within it. Mineral extraction has taken place in Cornwall since the Bronze ·age (Edmunds et al., 1975). Since then the county, including areas within the Loe Pool catchment have been worked for various ores, particularly Cassiterite (stannous oxide). The level of mining activity within Cornwall rose sharply as the demand for Pewter grew in the 17th century. Mining was of great importance from then until slumps occurred in the 1880's and 1920's. The decline in the extraction industry was brought about principally by exploitation of cheaper overseas ore deposits. In the Loe Pool catchment over 30 mines are known to have operated in the last 150 years. Coard (in prep.) has detailed their location and periods of operation. Most mining activity did not involve primary extraction but reworking, and then reworking again of alluvial deposits and mine spoil tips. The two periods of greatest mining activity were from 1845-1880 and 1908-1938.

Mining operations had a considerable influence on sediment formation in Loe Pool. The River Cober was used to supply power to machinery, to separate waste from ore and to carry waste away. Coard (in prep.) cites several authors who describe the River Cober and Loe Pool being polluted by mine effluent. The Cober was considered to be unpotable owing to the high tin content. Both the River and Pool were tinted a reddish hue from haematite waste. Records show discolouration occurred in the 1850's, 1870's, 1890's 1920's and 1930's (Coard in prep.).

The mining operations caused the deposition of large quantities of sand, silt and clay and have been a major factor in the silting up of Loe Pool. This is discussed in more detail in section 2.2. There is clear evidence of this debris in the sediment column (section 2.3). The red clay does have a beneficial use as a sedimentary marker in this study (Plate 1). Coard (in prep.) notes that mining operations probably ceased in the catchment by 1938 or 1939. There has been no commercial mining since then.

The changes in land use have influenced the rates of erosion from the catchment. Considerably more material was eroded from the catchment during periods of intense mining activity (Table 3).

2.1.6 Settlements

The catchment includes two major settlements, and has a total population of about 15,000 people. The largest is the town of Helston with a current population of about 12,000. These figures increase in the summer with the tourist influx. Helston has grown

Period	Erosion Rate $t/km^2/yr$	Main or Dominant Catchment Activity
1938-81	12	Agriculture
1937-1938	361	Intensive Mining & Agriculture
1930-1936	421	Intensive Mining & Agriculture
1860-1920	174	Mining & Agriculture

Table 3. Estimated Erosion Rates in Loe Pool Drainage Basin
1860-1981
(Source, O'Sullivan et al., 1982).

Year	Approximate Population*
1801	2-3,000
1901	4-5,000
1981	12,000

*Figures vary with the change in boundary for the
town of Helston

Table 4. Growth of Population in Helston, Cornwall
(Source, Coard, in prep.).

considerably over the last 200 years (Table 4).

During this time the effluent discharged from the town has increased. The history of sewage disposal in the Loe Pool catchment has been outlined by Coard (in prep.) The following is a summary of his data:

Pre 1875   Use of ash pits, earth closets and in town, soil closets which were emptied at a refuse tip.

1875-1930   Building of sewer system to discharge waste to the River Cober.

1930   Building of Helston sewage works above Loe Pool.

1950   Enlargement of Helston sewage works.

1970   Rebuilding and enlargement of Helston sewage works.

The sewage works treat the effluent for primary and secondary wastes but does not remove all phosphorus and nitrogen. The effluent discharged from the works enters the River Cober 200m above the inflow into the Pool.

The second major settlement is R.N.A.S. Culdrose. This was commissioned in 1947 and has increased in size since then. The population at the base is currently about 2,000-3,000 (Coard, in prep.). Some effluent from the station is treated before discharge to Carminowe stream, which flows into Loe Pool (Fig. 7). The rest is treated and piped out to sea.

The remainder of the population live in small villages and isolated farms where most sewage disposal is via septic tanks.

2.2 Loe Pool

2.2.1 Physical Characteristics of Loe Pool

The principal physical and hydrological characteristics of Loe Pool (Coard et al., 1983) are shown in Table 5. The lake's depth contours are illustrated in Fig. 9. The annual mean hydraulic residence time is given as 20 days; this figure is subject to strong seasonal fluctuations. In the summer months, the mean hydraulic residence time increases and in the winter months it decreases as a function of streamflow.

The lake currently covers 55.6 ha. In the past the lake occupied a far larger area (Coard, in prep.). From research of historical documents, Coard (in prep.) has shown that the area of Loe Pool has been reduced from 66 hectares in 1848 to 55.6 hectares at the present time. The greatest period of lake infill occurred from 1906 to 1940, when the lake was reduced in area by 14.4%. The primary cause of this being deposition of mine waste.

In the Cober valley to the north of Loe Pool, there is currently a large area of swamp-carr on an area that was formerly open water. There, sedimentation has been aided by the colonization by vegetation of a large area around the River Cober inlet.

The Pool is fed by the River Cober which supplies approximately 90% of the inflow (Toy, 1934), the Penrose, and Carminowe streams contribute the balance. Both the River Cober and Penrose Stream flow into the northern area of the lake and the Carminowe stream

Table 5. Principal Physical and Hydrological Characteristics
of Loe Pool.
(Source, Coard et al., 1983).

Latitude	50° 04' N
Longitude	5° 17' W
Altitude	4 m. O.D.
Area (A)	55.6 ha.
Length (L)	1.25 km.
Breadth (B)	250 m.
Maximum depth (Z_{max})	10.67 m.
Mean depth $(\bar{Z})$	3.47 m.
Relative depth (Z_r)*	1.27
Volume (V)	$1.93 \times 10^6 \; m^3$
Mean hydraulic residence time	20 days
Area of drainage basin (D)	50 km^2
D/A	98.9

$$*Z_r = 50 \; Z_{max}\sqrt{\pi} \; (\frac{1}{\sqrt{A}})$$

--2-- Depth in metres

N

0   250 m

Drainage 'adit'

Loe Bar
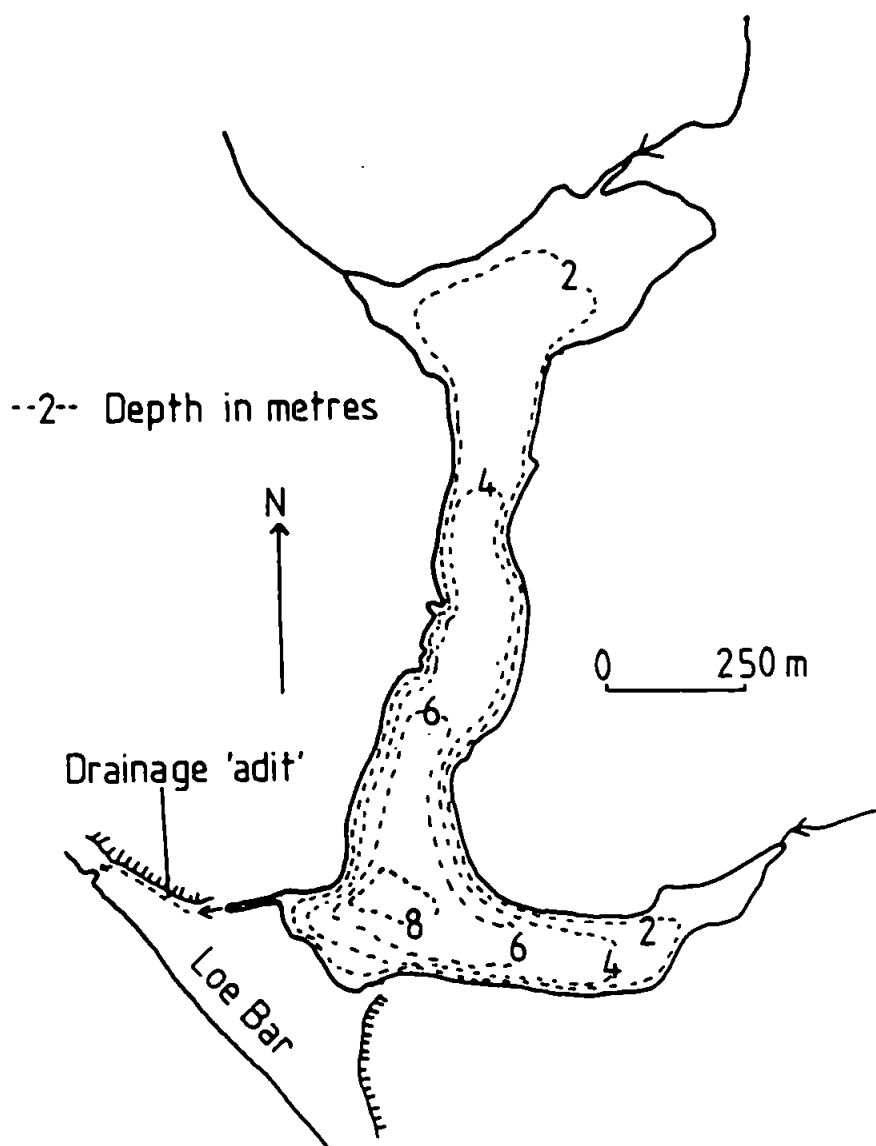
Figure 9. Depth contours of Loe Pool
(from Simola *et al*., 1981).

flows into the east arm (Fig. 7).

2.2.2 Trophic Status

Analysis of sediment has indicated that Loe Pool has become increasingly eutrophic throughout the 20th Century. Evidence for this has been found from analysis of sedimentary organic matter, chlorophyll degradation products, total phosphorus, sterols, diatom and cladoceran remains in sediment (Coard et al., 1983). Analysis of sedimentary diatom remains has shown changes in lake flora during the 1940's and increasing eutrophication throughout the 1950's, 60's and 70's (Simola et al., 1981; Coard et al., 1983).

Direct limnological evidence of eutrophication is given by the occurrence of algal blooms in the early 1970's. A plankton survey by South West Water Authority in 1970 and 1972 found that "clean water algae" only occurred in the Carminowe inlet, whereas the Cober inlet was dominated by "polluted water algae" which formed blooms in mid summer (Coard, in prep.). Blooms of green or blue-green algae have also been recorded in 1975, 1976, 1978, 1979, 1981, 1982, 1983 & 1984 (Greaves pers. comm.). A current study by Greaves (in prep.) has found that phytoplankton populations are dominated by diatoms in Spring, the green algae Chlorophyceae in summer and cyanobacteria in late August and September.

A study by Lacey (in prep.) has investigated the nutrient loading on Loe Pool. The Pool is considered eutrophic, with the maximum nutrient levels occurring typically during June, July and August

(Lacey, 1983).

The lake has experienced oxygen stress throughout July and August in the bottom-waters. In the summer of 1983, thermal stratification developed and hypolimnetic waters below 8m were significantly depleted in oxygen($<$1.5%, 0.1mg/l; Greaves & Lacey pers. comm.).

O'Sullivan et al. (1984) suggested that thermal stratification, with the hypolimnion reduced in oxygen, may have occurred on a regular basis in the past when the lake was deeper. That is when the mean depth of water was 7m or more, compared with the current figure of 3.5m.

2.3 Loe Pool Sediment

There are several published accounts of the stratigraphy and selected characteristics of Loe Pool sediment (Simola et al., 1981, O'Sullivan et al., 1982, Coard et al.,1983; Cousen & O'Sullivan, 1984; O'Sullivan et al., 1984). The following sections will summarise the sediment stratigraphy and individual chemical and biological properties that have been studied.

2.3.1 Sediment Stratigraphy

The longest core obtained from Loe Pool was collected in the summer of 1983. A Russian Peat Sampler (Jowsey, 1966) was operated from a raft constructed of oil drums and scaffolding. The location of the sediment core site,(L), is shown in Figure 10. Core sections taken were 50 cm long, but collected at 25 cm intervals to ensure a

Cores collected from :
　site A
　M 1, LP 25, LP 31
　LP 32, LP 35
　site H
　LP 6
　site L
　Longest core

H ⟍ 'Head of Neck'

L˙
A˙
×Southern Jetty
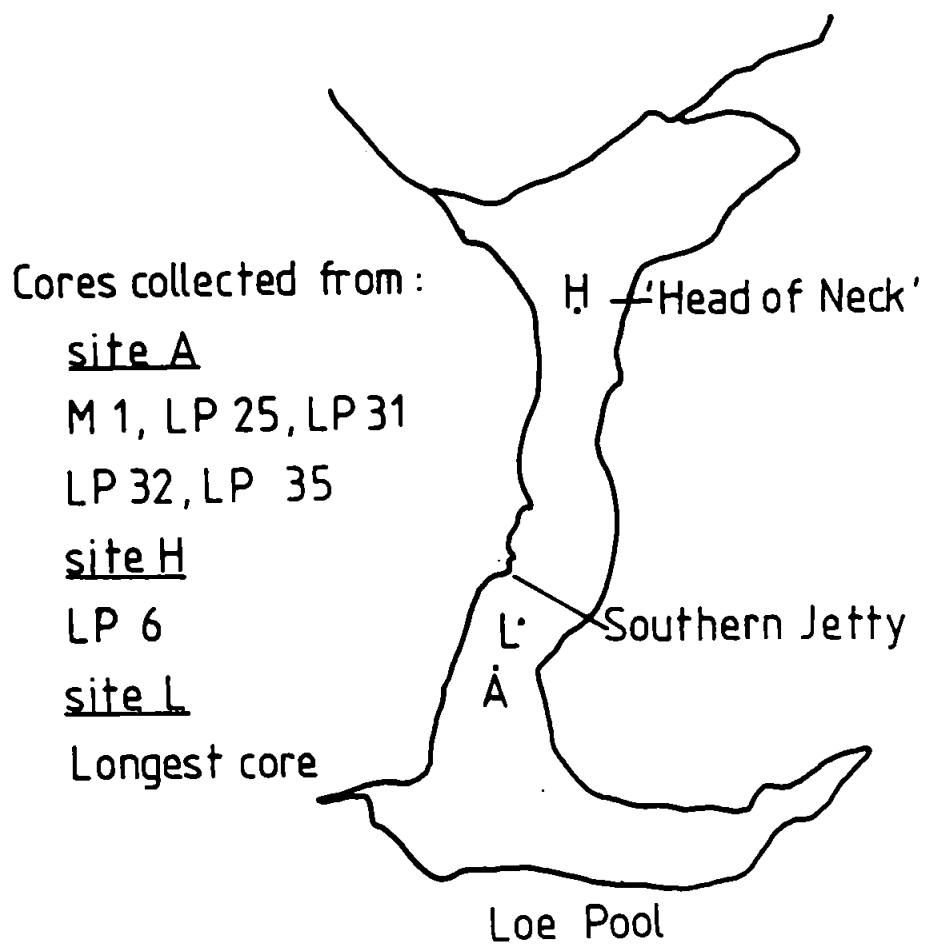
Loe Pool

Figure 10. Loe Pool showing location of coring sites.

continuous stratigraphy.

A summary of this stratigraphy is reproduced from O'Sullivan et al. (1984):

Depth of sediment	Description of sediment
0-20 cm	Dark brown watery clay-gyttja.
20-32 cm	Pink haematite clay containing two black laminations.
32-97 cm	Massive grey and dark grey clay.
97-282 cm	Regularly laminated black and grey clay, each pair c. 1-3 cm thick. Pink laminae replace grey at 144-145 cm, 151-152, 153-154 cm, 163-169 cm, 195-197 cm, 200-201 cm, 205 cm, 209-210 cm, 226-230 cm, 232-233, 235 cm and 237-238 cm.
282-286 cm	Yellow-brown clay.
286-326 cm	Further grey-black laminations.
326-533 cm	Stiff brown clay with many fine and several prominent pale grey laminations.

This stratigraphy is illustrated with dates (Fig. 2). Previous work (Simola et al., 1981) from the nearby sampling site A, (Fig. 10), revealed the following sediment sequence:

Depth of sediment	Description of sediment
0-40 cm	Highly organic gyttja, with four or five pairs of light and dark brown laminations just below the sediment surface (0-5 cm),

the rest more homogenous.

40-120 cm   Irregularly laminated sequence containing red and grey clays alternating with darker layers.

120-300 cm   More regularly laminated sediment consisting of paired grey and black layers, average thickness 3 cm per pair.

The results concurred with those for the deeper core. Small differences in depth of stratigraphic units are caused by variations in rates of sediment deposition at each sample site.

Various sections (0-72 cm, 40-110 cm, 194-206 cm, and 230-242 cm) from the core reported by Simola et al. (1981) were examined in detail. In all sediment samples studied, diatoms were found to occur in rhythmically repeating sequences. These were attributed to the seasonal growth and deposition of algae species.

The top brown gyttja had poorly defined laminations in the upper 5 cm of sediment only. Below this the sediment was bioturbed. Analysis for Cs-137 showed that the highest concentration (associated with the maximum environmental value for 1963 (Pennington, Cambray & Fisher, 1973)) was at a depth of 14-16 cm. This peak was approximately half way down the brown clay-gyttja which suggested that this sedimentary unit had accumulated since approximately 1940.

The second stratigraphic unit from 40-120 cm contained red and grey clays, with some darker layers. The authors concluded from diatom evidence that this 80 cm accumulated in only 7 years. This massive sediment layer was attributed to very active mining within the catchment area up to 1938. The top of this stratigraphic unit

is marked by a very pronounced pink lamination, which is taken to have been deposited at the end of the mining period. The pink haematite clay has only been found in the catchment at the Porkellis Mine which ceased operations in 1938. This pink clay layer can, therefore, be dated at 1938 from documentary records. This date is in broad agreement with the 1940 date estimated from 137-Cs data for the base of the brown gyttja.

Below the massive grey clay layer is a sequence of black and grey laminations. These are recorded to a depth of 280 cm by Simola et al. (1981). Sections of this sequence were analysed in detail by the tape peel technique of Simola (1977). Simola et al. (1981) reported that the black and grey laminations were annual in nature, the black layer representing the summer months and the grey layers the winter.

2.3.2 Sedimentation Patterns Across the Lake Bed

Many sediment sequences cored from Loe Pool have suggested that sediment stratigraphy is similar across the lake bed, but that each stratigraphic unit has a different thickness depending on core location. To test this observation, a multiple series of Mini-Mackereth cores were taken across the whole lake bed (O'Sullivan et al., 1982). The depth of the brown gyttja was measured from sediment-water interface to the base of the gyttja marked by the pink haematite lamination. A map showing depth contours for the thickness of the brown gyttja was drawn (Fig. 11). There is a clear deltaic deposition effect around the inflow of the Cober and in the bay of the Penrose stream. An unpredicted increase
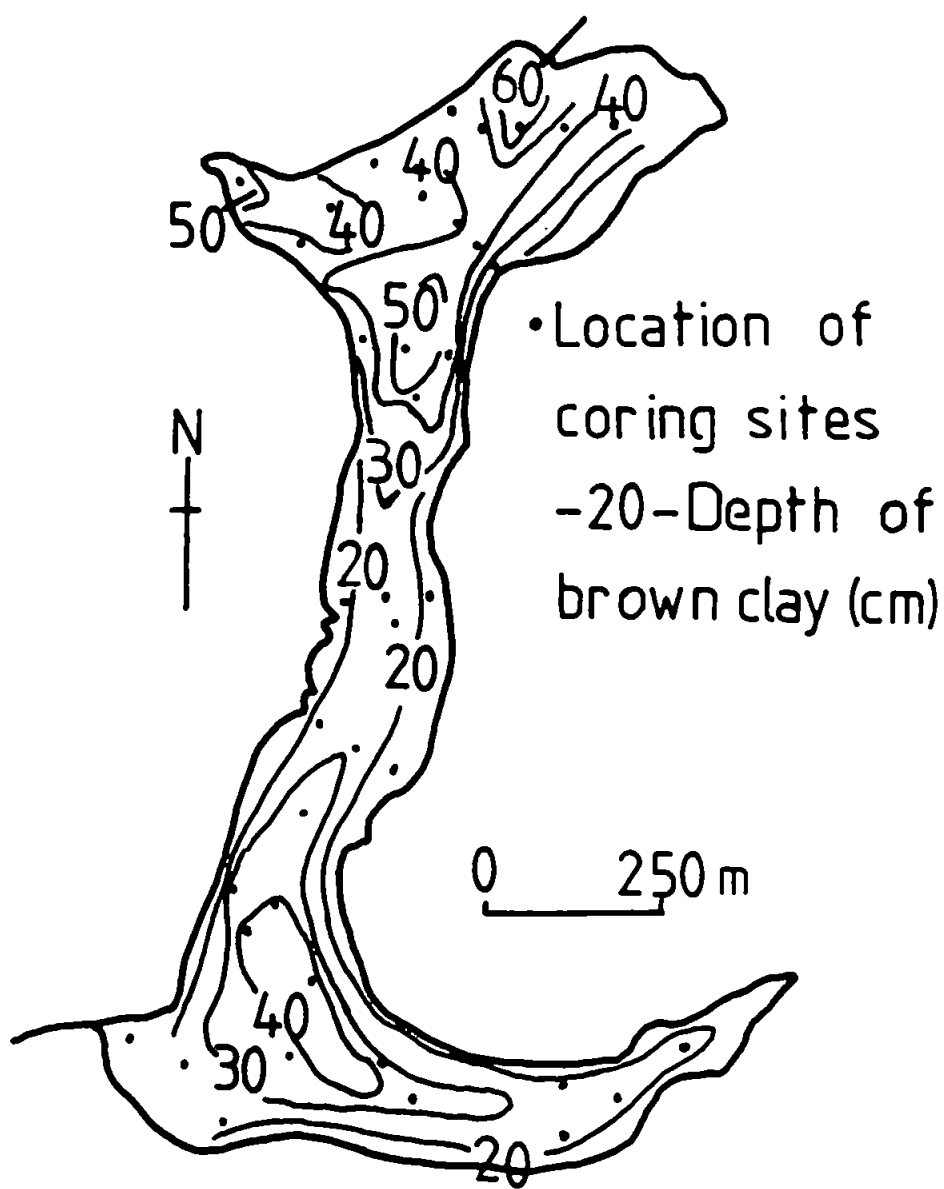
Figure 11. Isopach map of the brown clay sediment of Loe Pool
produced by multiple-coring (from O'Sullivan *et al.*,
1982).

in sediment deposition occurs at the north end where the lake narrows. Throughout the "long thin" section of the lake sediment deposition is lower but increases towards the deepest point. This may be a function of sediment focussing as described by Likens & Davis (1975).

O'Sullivan et al. (1982) concluded that the lake's morphometry influenced the rate of sediment deposition at any site. In addition, it was considered that the deltaic section had a higher proportion of allochthonous material relative to autochthonous material than found in other parts of the lake. Core location should, therefore, be considered when discussing results.

2.3.3 Chemical and Physical Properties of Loe Pool Sediment

The sediment of Loe Pool has been analysed chiefly by undergraduates for selected chemical and physical properties. The results of this work are summarised in the paper by Coard et al. (1983). The salient points are: From the top brown gyttja deposited between 1940 and the present day, loss on ignition as a percentage of dry weight increased from 3-4% to 15-20%, sedimentary chlorophyll increased from approximately 10 to 80-120 units per gramme dry weight, and phosphorus increased from 1 to 5-7 mg/g dry weight.

Analysis of sterols revealed an increase of $100\mu g/g$ dry wt. in the red and grey clays to over $350\mu g/g$ dry wt. in the surface sediment. This apparent decrease with depth may be caused by degradation of sterols with time.

Care needs to be taken with the interpretation of organic

components per gramme dry weight because they are based on the assumption that the % dry weight remains the same. If the % dry weight was to increase, for example, as a result of input of allochthonous mine waste, then the concentration of organic component would be reduced. This reduction would be a function of dilution of the organic component by minerogenic material. This is particularly important when comparing concentrations of components between different types of sediment.

The tin concentration of Loe Pool sediment has been studied by X-ray fluorescence spectrometry (Ø'Sullivan et al., 1984). In the lowest section of brown clay analysed (c. 326 cm to 533 cm) the maximum concentration was 200 ppm. In the overlying black/grey laminated sediment (c. 97cm to 326 cm) the tin concentration was in the range of 600-3,600 ppm, with peaks at 195-205 cm, 235-245 cm, and 285-295 cm which date from 1885, 1870 and 1835 respectively. These high concentrations of tin may be correlated with historical records of increased mining activity (Coard, in prep.).

Chapter 3 Selected Physical and Chemical Properties of

Lacustrine Sediment

Many physical and chemical techniques have been used in the

investigation of lake sediments (Mackereth, 1966; Strickland &

Parsons, 1972; Cranwell, 1978;   Bengtsson, 1979; Dean, 1981;

Oldfield et al., 1985). This chapter presents a review of

selected techniques together with examples of their applications in

palaeolimnology. In addition, there is a brief discussion of their

potential use when applied to the analysis of laminated sediment.

3.1 Photographic Evidence

Photography (colour, black and white, infrared, x-ray) has been

frequently used to document and study laminated sediment (Tolonen,

1978; Saarnisto, 1979; Simola et al., 1981;   Coard et al.,

1983). Photographs may be used to store   information for counting

laminations and for recording the colours and thickness of each

lamination within a sequence (Renberg, 1978a; Renberg, 1981b).

3.2 Dry weight, Loss on Ignition and Combustion Residue

Accurate determination of dry weight, loss on ignition and

combustion residue are essential for expression of results "per

gramme" dry weight, loss on ignition and minerogenic material.

Additionally the properties of loss on ignition and combustion residue have been used to illustrate variations in sediment quality caused by climatic or cultural changes in the catchment over periods of hundreds to thousands of years (Anthony, 1977; Renberg, 1978a; Renberg & Segerström, 1981). For example, at the Lake of the Clouds (Anthony, 1977), loss on ignition results were used to indicate % organic matter (Fig. 12). Anthony reported an increase on loss on ignition from 5% in the basal silt deposited approximately 11,000 years ago to 35-40% in the most recent sediment. This was interpreted as illustrating an increase in the lake's productivity with time.

Changes in dry weight, loss on ignition and combustion residue may also vary on a seasonal basis as a response to changes in the quantity or quality of sediment being deposited. Loe Pool probably has a maximum input of minerogenic material during periods of high stream flow in the winter months and conversely a maximum input of autochthonous organic matter during the highly productive summer months. It is possible that such variations may produce detectable differences in loss on ignition and combustion residue values from sediment deposited in the summer and winter laminations.

3.3 Introduction to Selected Magnetic Variables

Lake sediments exhibit a range of magnetic properties as a result of the electron and orbital spins within the atoms of the mineral component (Oldfield et al., 1985). The close relationship between the movement of a magnetic field and the production of an

- 43 -
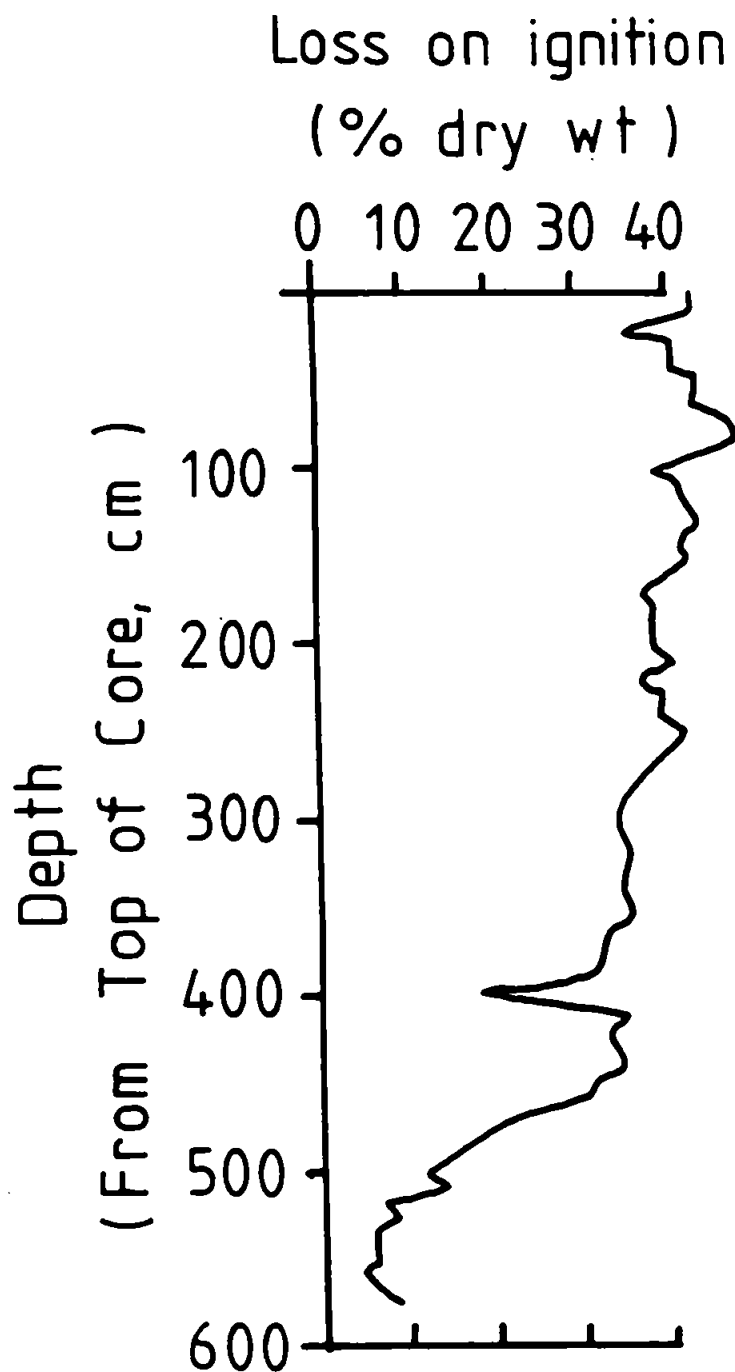
Figure 12. Profile for loss on ignition at 650°C
in Lake of the Clouds sediments
(from Anthony, 1977).

electrical current, together with the development of sensitive electrical equipment, has allowed the measurement of several magnetic parameters of lake sediments (Thompson, 1973; Thompson & Kelts, 1974; Thompson & Oldfield, 1978; Rummery et al., 1979; Thompson et al., 1980; Dearing, Elner & Happey-Wood, 1981; Dearing, Maher & Oldfield, 1984; Oldfield & Appleby, 1984).

Magnetic properties may be categorised into two types (Oldfield et al., 1985). Those which arise from the effect of the Earth's magnetic field on the sample some time in the past and those which independent of the Earth, exhibit a field caused by their mineral assemblage. The former type, termed Natural Remanent Magnetism, is not applied in this study. The latter type has been termed mineral magnetic properties and will be considered in the following text. There are four main forms of magnetic behaviour that occur within minerals. The information presented below describes each of these and was condensed from a paper by Oldfield et al. (1985).

Every mineral shows some form of magnetic behaviour, this results as a combination of that mineral's diamagnetic, paramagnetic, ferrimagnetic and anti-ferromagnetic properties.

Diamagnetic and paramagnetic minerals both produce a weak resultant dipole moment when placed in a magnetic field. These two mineral properties are distinguished according to their direction of alignment with respect to the field. The alignment of paramagnetic minerals is in the same direction and diamagnetic minerals in an opposite direction, to the magnetic field. Examples of diamagnetic minerals include water, limestone, organic matter and some silicate materials. Paramagnetic minerals are usually only significant when there are high concentrations of iron and/or

manganese compounds which are not in the ferrimagnetic or anti-ferromagnetic form.

Ferrimagnetic minerals gain a strong positively-aligned magnetic moment when placed in a field, part of which they retain when removed from it. Common ferrimagnetic minerals are magnetite (Fe_3O_4) and maghemite (Fe_2O_3).

Anti-ferromagnetic minerals also acquire a positively-aligned magnetic moment when placed in a field, some of which is retained on removal. The anti-ferromagnetic moment is much weaker than the ferrimagnetic moment. Haematite (Fe_2O_3) is an example of a mineral displaying anti-ferromagnetism.

In any given mineral assemblage there will be a combination of the above properties. The assemblage can best be characterised by subjecting it to a number of magnetic measurements. Variables commonly used are magnetic susceptibility (χ), saturated isothermal remanent magnetism (S.I.R.M.) and coercivity of isothermal remanent magnetism.

Magnetic susceptibility is the ratio of induced magnetism to applied field or more simply a measure of the magnetizability of a sample (Thompson, 1979). Susceptibility is principally a function of the volume of ferrimagnetic minerals present, but also depends upon grain size and shape of the magnetic particles, their spontaneous magnetism, internal stress and other non-intrinsic parameters (Thompson et al., 1975). The magnetic properties of susceptibility and S.I.R.M. can be represented graphically by a hysteresis loop (Fig. 13).

The property of isothermal remanent magnetism (I.R.M.) is defined as the magnetic moment induced, in and retained by, a sample after
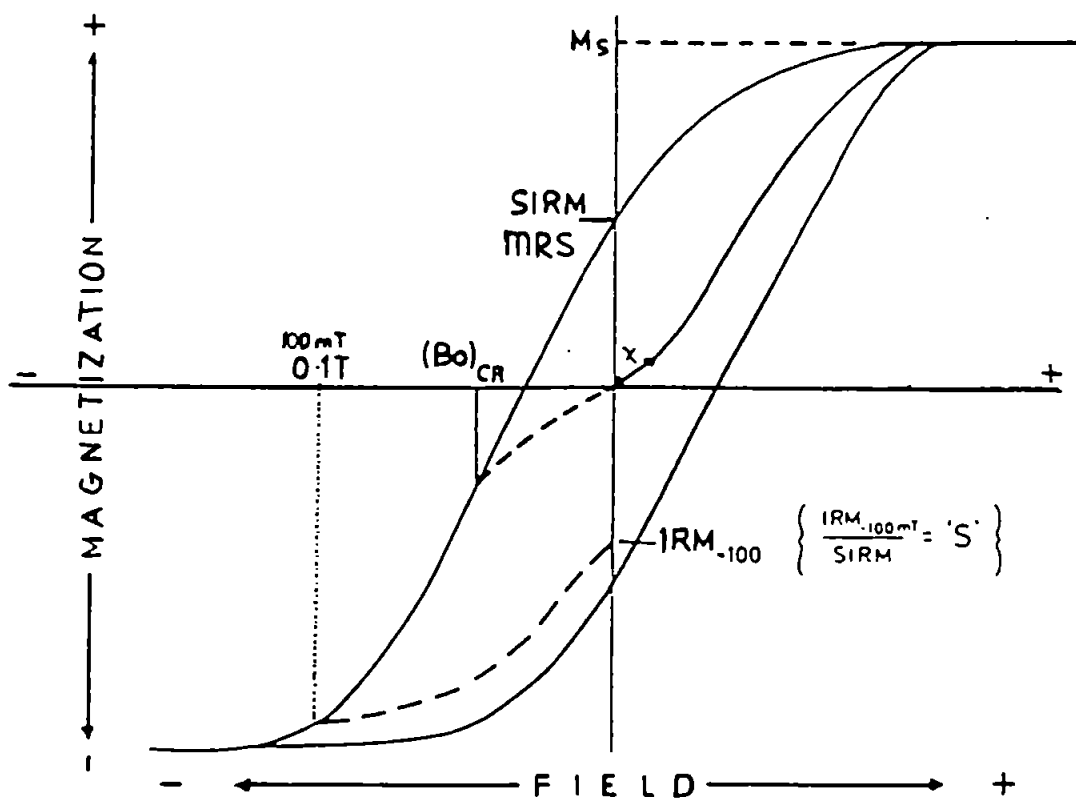
Figure 13. Hysteresis loop
(from Oldfield et al., 1985).

it has been placed at room temperature in a magnetic field (Thompson, 1979). I.R.M. increases in a non-linear fashion with the strength of the applied field until S.I.R.M. is reached. Beyond this level an increase in the field will not lead to any increase in I.R.M. (Thompson, 1979), which is illustrated in Figure 13. A mineral placed in a positive field will increase in magnetization until saturation magnetism (Ms) is reached. On removal from the electromagnet the field returns to zero and the magnetization of the sample declines along a different path to MRS. This is the S.I.R.M. of that mineral assemblage.

The property of S.I.R.M. varies with the type and size of magnetic mineral. In a suite of samples in which a single type of magnetic mineral is dominant or in which the magnetic minerals occur throughout in constant proportion there will be a direct linear relationship between magnetic susceptibility and S.I.R.M.

The magnetic susceptibility is a function of the gradient of the line expressing magnetism versus field strength (Fig. 13). Typically the line, would be quite steep for ferrimagnetic minerals such as magnetite and relatively shallow for the anti-ferromagnetic haematite (Fig. 14).

The S.I.R.M./magnetic susceptibility ratio reflects the concentration of magnetizable material, the grain size and mineralogy. Magnetic grain size is described in terms of domains. The number of domains present is a function of crystal type. Crystals greater than 1-2μm undergo a large loss of magnetization on removal from a saturated field and subsequently have a low S.I.R.M. and S.I.R.M./magnetic susceptibility ratio. This is known as a viscous loss of remanence (Oldfield et al., 1985). In

HAEMATITE

$\frac{SIRM}{\chi}$ high

SIRM

$(Bo)_{CR}$

χ

100

100

M

H (mT)

$(Bo)_{CR} > 200\ mT\ (0.2\ T)$

$\frac{IRM-100\ mT}{SIRM} \sim +0.9$

MAGNETITE

$\frac{SIRM}{\chi}$ low

SIRM

$(Bo)_{CR}$

χ

100

100

M

H (mT)

$(Bo)_{CR} \sim 50\ mT$

$\frac{IRM-100\ mT}{SIRM} \sim -1.0$
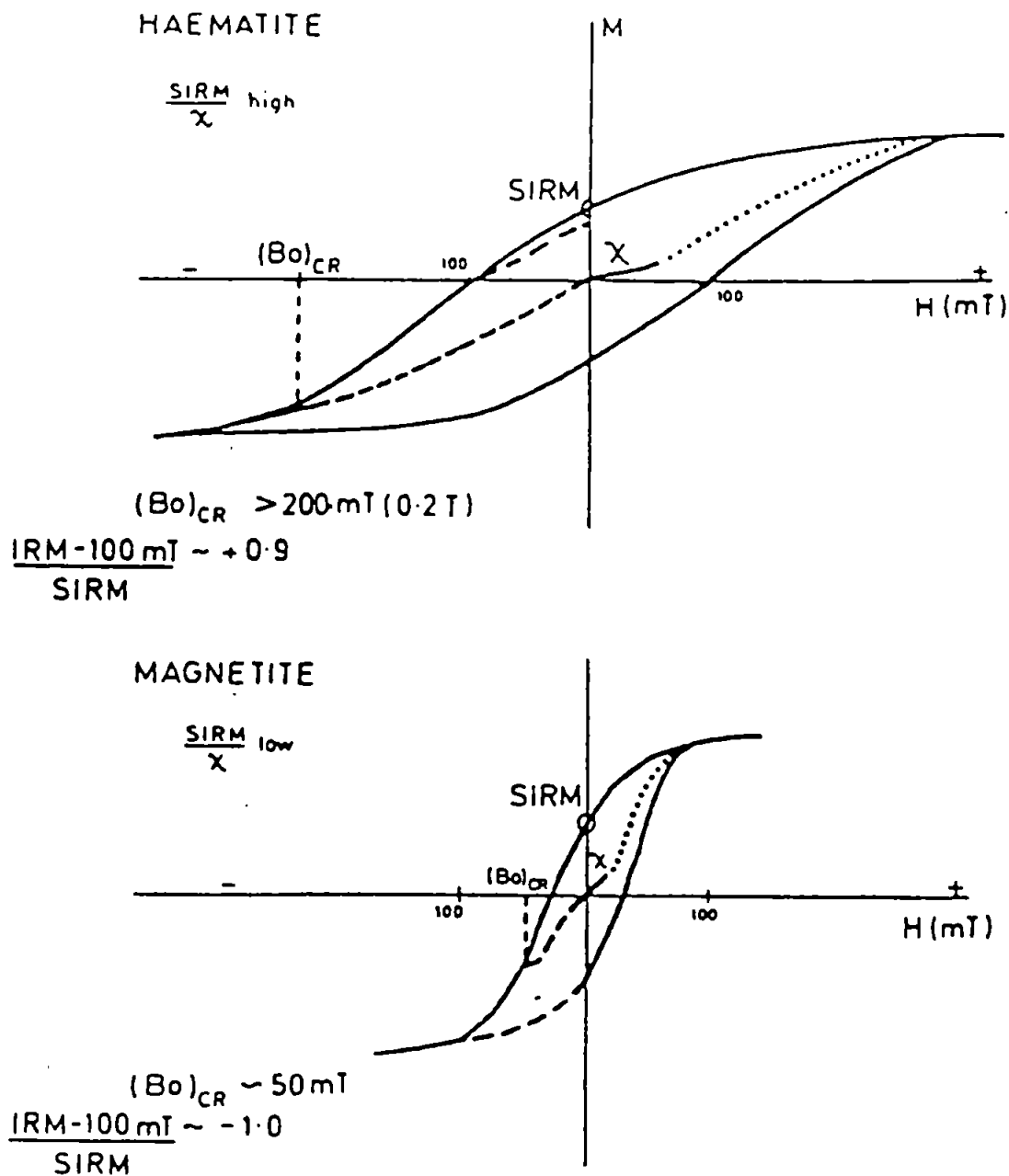
Figure 14. Generalised hysteresis loops for haematite
and magnetite minerals
(from Oldfield et al., 1985).

crystals of approximate size 0.05-0.1µm, each grain forms its own domain. In such stable single domain (S.S.D.) grains the loss of moment on removal from a field is at a minimum, so consequently the S.I.R.M. and S.I.R.M./magnetic susceptibility ratio are at their highest (Oldfield et al., 1985). Grains smaller than 0.03µm lose any magnetic moment gained in a strong field by thermal randomization. These grains are known as superparamagnetic. They have zero S.I.R.M. though they may have a high susceptibility for their volume.

Grains with a size between S.S.D. and superparamagnetic are termed viscous. They have a characteristic delayed response to changes in magnetic field. This is known as a quadrature or out of phase component (Oldfield et al., 1985).

By taking the saturated sample and demagnetising it in a reverse field the magnetization decreases (Fig. 13). The coercive field or coercivity of S.I.R.M. (Bo) C.R. is the reverse field required to reduce S.I.R.M. to zero (Oldfield et al., 1985). Sometimes a partial backfield is induced and measured in order to plot:

$$\frac{\text{I.R.M.}}{\text{S.I.R.M.}}$$

This is frequently done using a backfield of 0.1 Tesla (1,000 Oersteds):

$$\frac{\text{I.R.M.-0.1T}}{\text{S.I.R.M.}}$$

The measurement is described as the S ratio.

The S ratio and S.I.R.M./magnetic susceptibility ratio are independent of concentration. They may be used to distinguish between ferrimagnetic (e.g. magnetite) and anti-ferromagnetic (e.g. haematite) mineral assemblages as illustrated in Fig. 14.

3.3.1 Application of Selected Magnetic Properties of Lake Sediment

At Llyn Goddionduon in Wales, magnetic susceptibility has been used to correlate and to aid quantification of sedimentation rates. (Bloemendal et al., 1979). Dearing et al. (1981) used magnetic susceptibility measurements to distinguish between sediment derived principally from channel erosion and from inwash of slate debris at Llyn Peris, Wales (Fig. 15). High values were produced from channel erosion and lower figures from the slate material. These results were linked with land-use records and pollen and pigment data, together with a reconstructed history of erosion rates to describe the erosional effects of mining, quarrying, overgrazing and recent construction work.

The magnetic susceptibility of sediment trapped over a period of one year was correlated with the rainfall to show the link with channel erosion (Dearing & Flower, 1982). Björck, Dearing & Jonsson (1982) measured the magnetic susceptibility of sediment deposited in a Swedish lake. They used the evidence to identify the time of the lake's isolation, and highlighted changes in the climate and
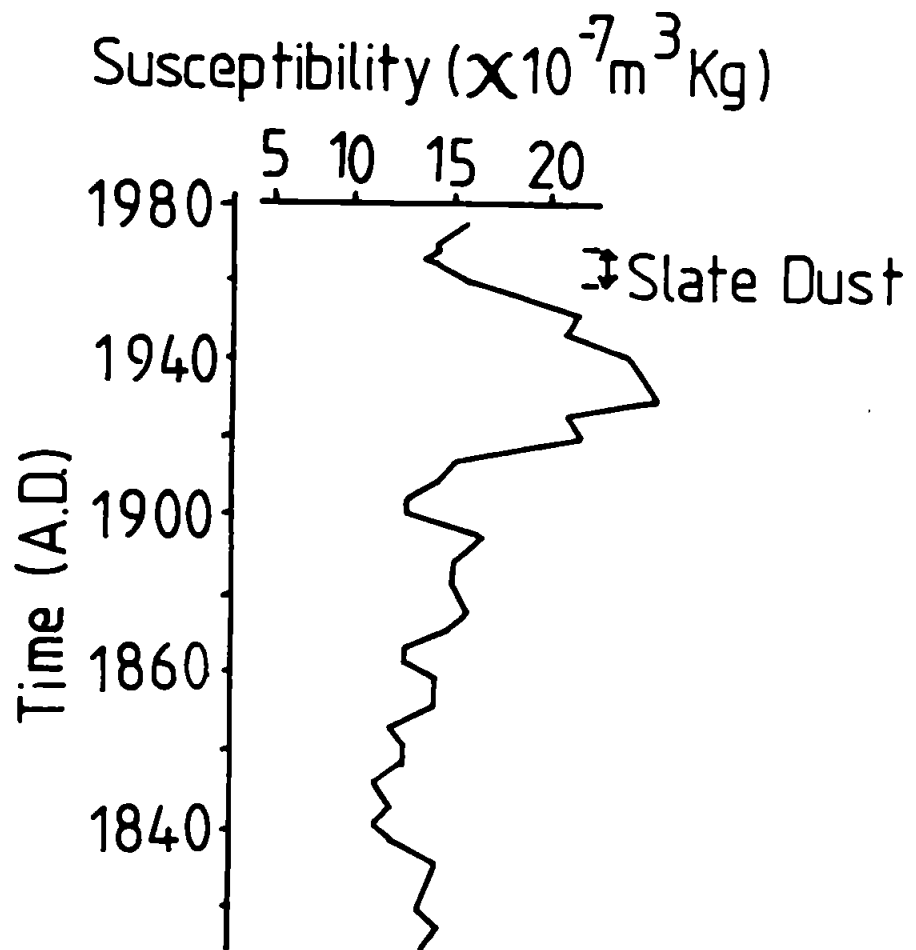
Figure 15. Depth profile of Magnetic Susceptibility
from c. 1760-1976 from Llyn Peris
(source Dearing et al., 1981).

rates of erosion with time. In South West England magnetic susceptibility, S.I.R.M. and coercivity of I.R.M. were used to identify the main source of suspended stream sediment (Oldfield et al., 1979).

By analysis of the Loe Pool sediment for the variables magnetic susceptibility and S.I.R.M. and subsequent calculation of the S.I.R.M./magnetic susceptibility and S ratio, it may be possible to detect differences between the seasonal laminations. This is because the summer and winter laminations were deposited under conditions of low and high river flow respectively. In addition, the main magnetic mineral assemblages may be identified which could give an indication of sediment source.

3.4 Analysis of metals

The analysis of metals has been widely used by palaeolimnologists in order to investigate past events within a lake and its drainage basin. Applications of such analysis include investigation of lake redox conditions (Mackereth, 1966), pollution events (Renberg & Segerström, 1981) and the intensity of erosion from a catchment (Mackereth, 1966).

This introduction to the analysis of lacustrine sediment will initially present information on techniques used to extract elements. The applications of elemental analysis in lake sediment will be reviewed. Finally, an outline will be given of the potential that these techniques offer in the investigation of the annually-laminated sediment formed in Loe Pool.

3.4.1 Techniques of Extraction

Various techniques have been used to extract elements from lake sediment. There are perhaps nearly as many methods as there have been papers published on the subject. This lack of uniformity makes it difficult to compare concentrations of elements from lake sediment analysed by different workers. However, the extraction techniques that are used may be grouped into categories based on the source of the material and its ease of extraction. Engstrom & Wright (1984) have summarised four categories as follows :

1) **Interstitial** and **extractable ions**, which are those metals that may be dissolved in pore waters or adsorbed onto sediment particles. Extraction can be by centrifugation (Haswell, 1983), squeeze filtration (Manheim, 1966) or by mild chemical extractants, for example, 1.0 M ammonium acetate (Jackson, 1958) or 0.5 M acetic acid (Allen et al., 1974).

2) **Biogenic silica**, which contains mainly amorphous silica from diatom frustules. This may be extracted by alkaline dissolution, for example, 0.2 N sodium hydroxide (Werner, 1966).

3) The **authigenic fraction** which consists of those elemental associations formed within the lake. For example, biochemically precipitated carbonates, metal oxyhydroxides, sulphides, phosphates and adsorbed or co-precipitated elements. These may typically be extracted with 0.3 M HCl, pH 3 or pH 7

citrate–dithionite or acetic acid–hydroxylamine solutions (Malo, 1977), or 1.0 M hydroxylamine hydrochlorate in 25% acetic acid (Chester & Hughes, 1967).

4) The allogenic fraction which . comprises largely of mineral particles resulting from the erosion of catchment soils. To extract this fraction a "total" digestion technique is employed using either fusion, for example lithium metaborate (Suhr & Ingamells, 1966), or strong acid such as a mixture of hydrofluoric and perchloric acids (Allen et al., 1974).

It should be emphasised that elemental associations do not occur within such clear–cut categories and as such these divisions are rather artificial. However, in the analysis of metals from lake sediment the following extraction techniques are commomly used: 1) some type of weak acid/complexing agent solution to obtain the authigenic fraction, and 2) either a fusion or a strong acid method to liberate all extractable metals.

The concentration of elements within lacustrine sediment is a function of supply to, and processes within, the lake system. Table 6 indicates mean metal concentrations from lake sediment and shale.

The following section reviews studies of elements in lake sediment and some of the applications of these data in palaeolimnology. The information is principally from the reviews of Mackereth (1966), Engstrom and Wright (1984) and references therein.

Metal	Metal contents of Pelitic sediments		Major influencing factors			
	Average Shale	Lacustrine deposits range for 90% of data n = 74	Bedrock lithology		Ca-Mg absent n = 50	Carbonates present n = 6
			granitoid n = 10	gabbroid n = 2		
Iron	46700	43000(12000-69000)	49000	58000	47100	16900
Manganese	850	750 (100-1800)	660	1100	902	475
Zinc	95	110 (45-220)	102	85	124	63
Nickel	68	66 (30-250)	69	1000	119	46
Copper	45	43 (20-80)	31	44	46	34
Lead	20	28 (8-75)	32	27	29	21
Cobalt	19	15 (3-40)	7	68	19	16

Table 6. Mean Metal Concentrations (ppm) and Major Influencing Factors in Lacustrine Sediments (Source, Förstner, 1977).

3.4.2 Iron and Manganese

The concentrations of many elements in lake sediment are controlled by both variations in erosion intensity from the land and redox conditions in the catchment and lake systems.

The physical state of iron and manganese are strongly influenced by the prevalent redox conditions. For example, iron may occur in an oxidised state $Fe(III)$ or the reduced $Fe(II)$. The $Fe(III)$ is relatively insoluble in lake water in comparison with the $Fe(II)$. In lake systems $Fe(III)$ is readily precipitated and $Fe(II)$ remains in solution. Manganese has a similar basic mechanism, the oxidised $Mn(IV)$ is readily precipitated from the lake system and in contrast the reduced $Mn(II)$ stays in solution. The form of the species is dependent upon the redox conditions existing in the catchment or lake system. The redox boundary reactions have been extensively reviewed by Davison (1985).

Sholkovitz (1985) notes that there are two important differences in the behaviour of iron and manganese in redox cycles. First, $Mn(IV)$ is reduced to $Mn(II)$ under higher redox conditions, that is greater concentrations of oxygen, than $Fe(III)$ is to $Fe(II)$. Secondly, he described that under the same conditions $Fe(II)$ is more rapidly oxidised to $Fe(III)$, than $Mn(II)$ is to $Mn(IV)$.

Mackereth (1966) illustrated the importance of catchment and lake redox chemistry by analysis of the iron and manganese concentration of sediment from Windermere and Esthwaite Water. The distribution of these elements in Windermere sediment and the Fe:Mn ratio are illustrated in Figures 16 & 18. Mackereth (1966) noted the decrease in Fe:Mn ratio in sediment deposited in Windermere after

the end of glaciation and attributed this to the formation of reducing soils in the surrounding drainage basin. He further suggested that the soils were sufficiently reduced that manganese was leached out of the catchment and deposited as manganese dioxide (Mn IV) in the lake. Iron transport would have been by physical erosion only as the soil conditions were not sufficiently reduced to mobilise the iron. This caused the increase in manganese concentration and subsequent decrease in Fe:Mn ratio (Figs. 16 & 18).

The concentration of both iron and manganese within sediment is also a function of the redox potential of lake waters. If the lake is aerobic, then both iron and manganese are readily precipitated. If reducing conditions occur with low pH and oxygen levels, first manganese, and if conditions become more severely reducing, then iron will enter solution.

Work by Mackereth (1966) showing the iron and manganese concentrations in the sediment of Esthwaite Water is illustrated together with the Fe:Mn ratio (Figs. 17 & 18). After glaciation and the development of organic soils, Mackereth noted fluctuations in the Fe:Mn ratio. He postulated that increases in the ratio were caused by periodic anoxic conditions which mobilized the manganese, but not iron into solution. This would have the effect of decreasing the precipitation of manganese and increasing leaching from the sediment-water interface, so increasing the Fe:Mn ratio.

Mackereth further suggested that it was possible to deduce whether changes in the Fe:Mn ratio were caused by changes in soil redox conditions and hence supply from the catchment, or, lake redox conditions which govern precipitation to the sediment. Where peaks
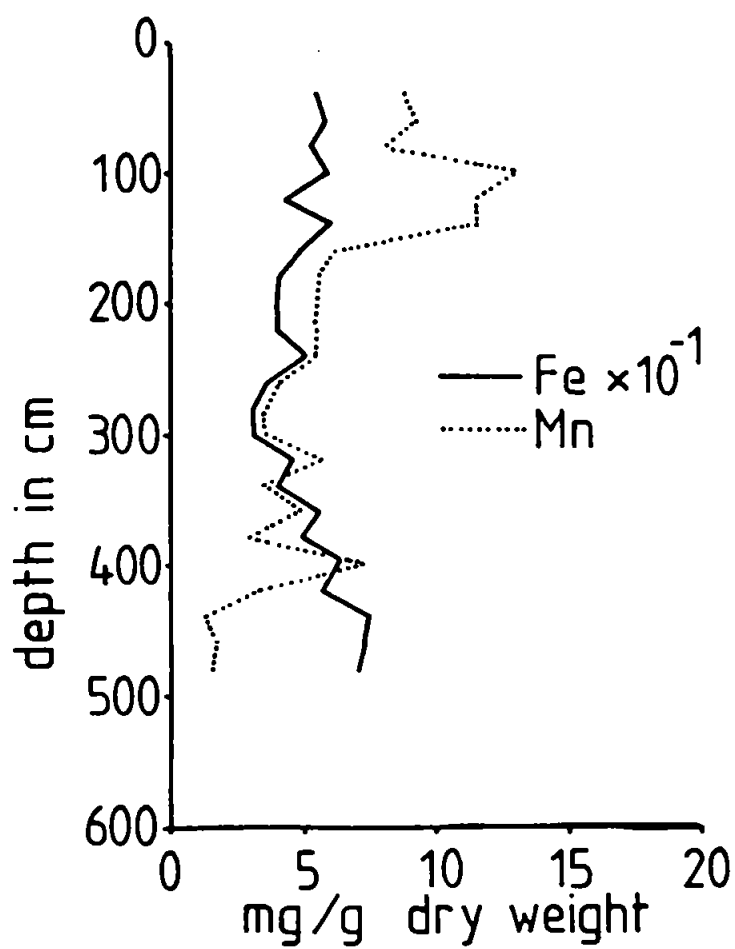
Figure 16. Concentration of iron and manganese in sediment from Windermere South Basin (from Mackereth, 1966).
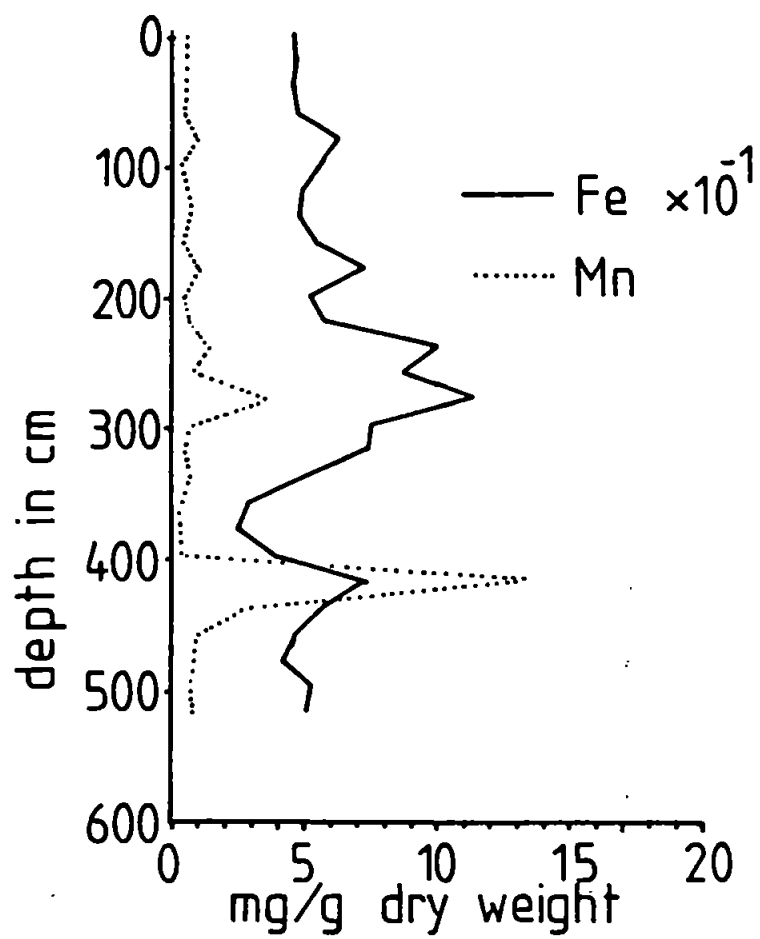
Figure 17. Concentration of iron and manganese in sediment from Esthwaite Water (from Mackereth, 1966).
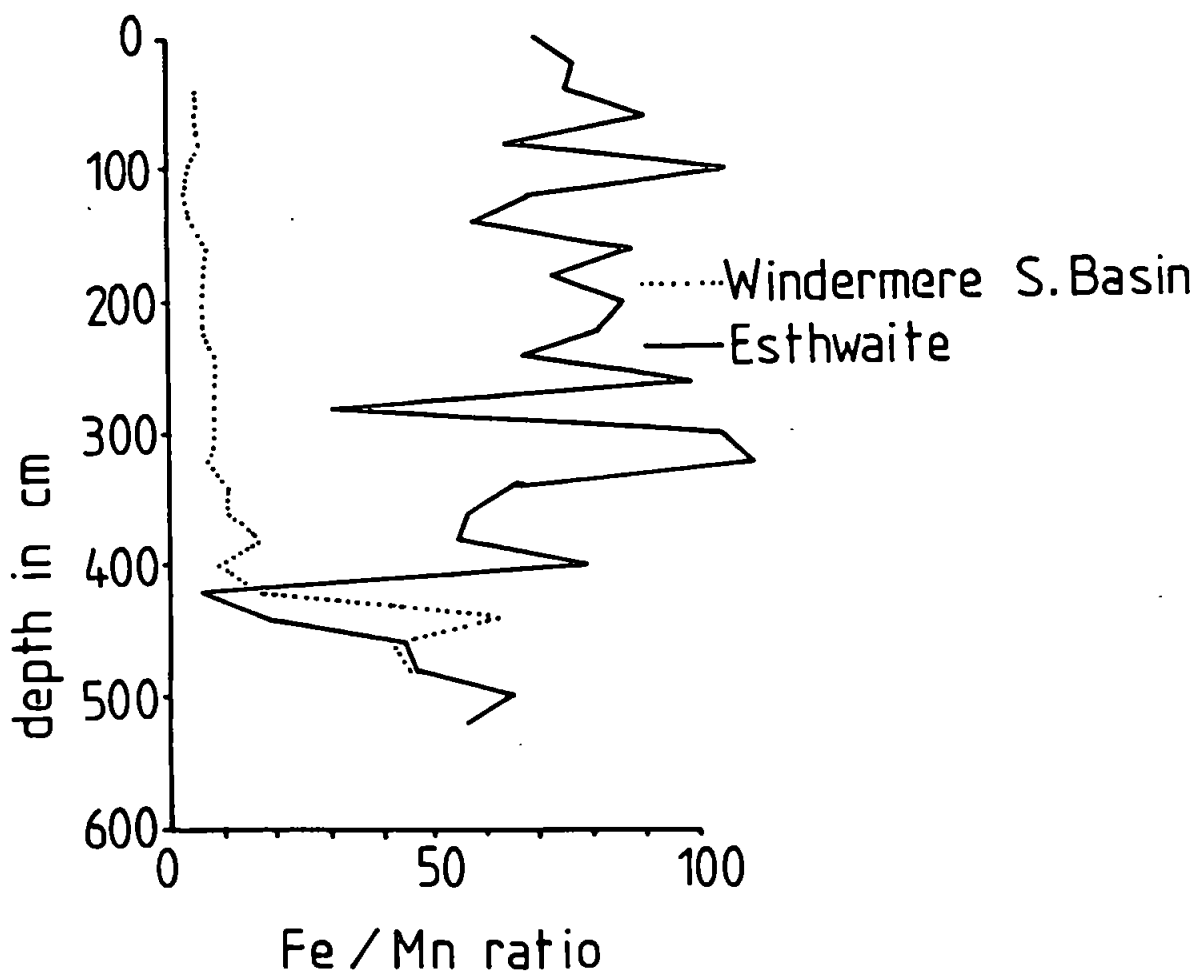
Figure 18. Variation with sediment depth of the ratio of iron to manganese in the sediments of Windermere South Basin and Esthwaite Water (from Mackereth, 1966).

in the Fe:Mn ratio are correlated with low iron concentrations, then this indicates reducing conditions at the sediment-water interface. This is because iron would be dissolved and so the iron concentration of the surface sediment would be lowered. Where peaks in the Fe:Mn ratio are correlated with peaks in sedimentary iron concentration, then soil redox conditions are most important. This is because both a high iron concentration and Fe:Mn ratio are indicative of low soil redox conditions in the catchment.

There are several other factors which influence the concentration of iron and manganese within lake sediment. Iron and Manganese are both associated with soil humus and in oxygenated waters can be deposited as hydrated oxides (Delfino & Lee, 1971) and coagulates of humic organic complexes (Nriagu & Coker, 1980). Iron and Manganese can also change in both concentration and ratio to each other across lake beds as a result of physical and chemical sorting. Syers, Harris & Armstrong (1973) found that the concentration of iron and manganese in sediment increased with water depth. This was attributed to selective transport of fine texture and low density iron and manganese precipitates by wave and current action. Jones & Bowser (1978) found that in Green Bay, Lake Michigan the Fe:Mn ratio decreased with distance from the river input. They suggested this was because of the more rapid precipitation of iron than manganese from the river source.

Iron and manganese are also thought to be transported towards deeper waters by chemical action. Engstrom, Swain & Kingston (1985) reported on the concentrations of iron and manganese and the Fe:Mn ratio from sediment deposited in Harvey's Lake, Vermont. Contrary to Mackereth's model, the Fe:Mn ratio was highest throughout the

presettlement period when the lake was probably aerobic and lowest in post settlement when profundal sediments were more reduced (Fig. 19). This was considered to be caused by transport of iron and particularly manganese into profundal regions under reduced conditions in the summer and subsequent deposition at the autumn turnover when the hypolimnion would be reoxygenated. This enhanced the concentration of both iron and manganese in the sediment under deeper water and because manganese is taken up into solution more readily than iron, lowered the Fe:Mn ratio. However it should be emphasised that such chemical transport depends upon a lake having an anoxic hypolimnion.

Other factors that can affect the iron and manganese concentration and subsequent Fe:Mn ratio in lake sediment include post-depositional migration (Carignan & Flett, 1981). The authors reported that elements can migrate upwards through reducing sediments to the oxygenated sediment-water interface where redeposition occurs. However, rapid burial can preserve enriched zones (Norton & Hess, 1980; Engstrom, 1983). Where sediments become even more reducing such that sulphides are formed, the sediment is likely to have an increased Fe:Mn ratio as manganese sulphide is more soluble than iron sulphide (Hutchinson, 1957).

Many factors are known to influence the concentration of iron and manganese in lake sediment. The careful use of these concentrations together with the Fe:Mn ratio and other limnological properties may allow the reconstruction of palaeo-redox conditions from the analysis of lake sediment.

At Loe Pool, there are the potential conditions for the occurrence of seasonal anoxia. There are currently periods of
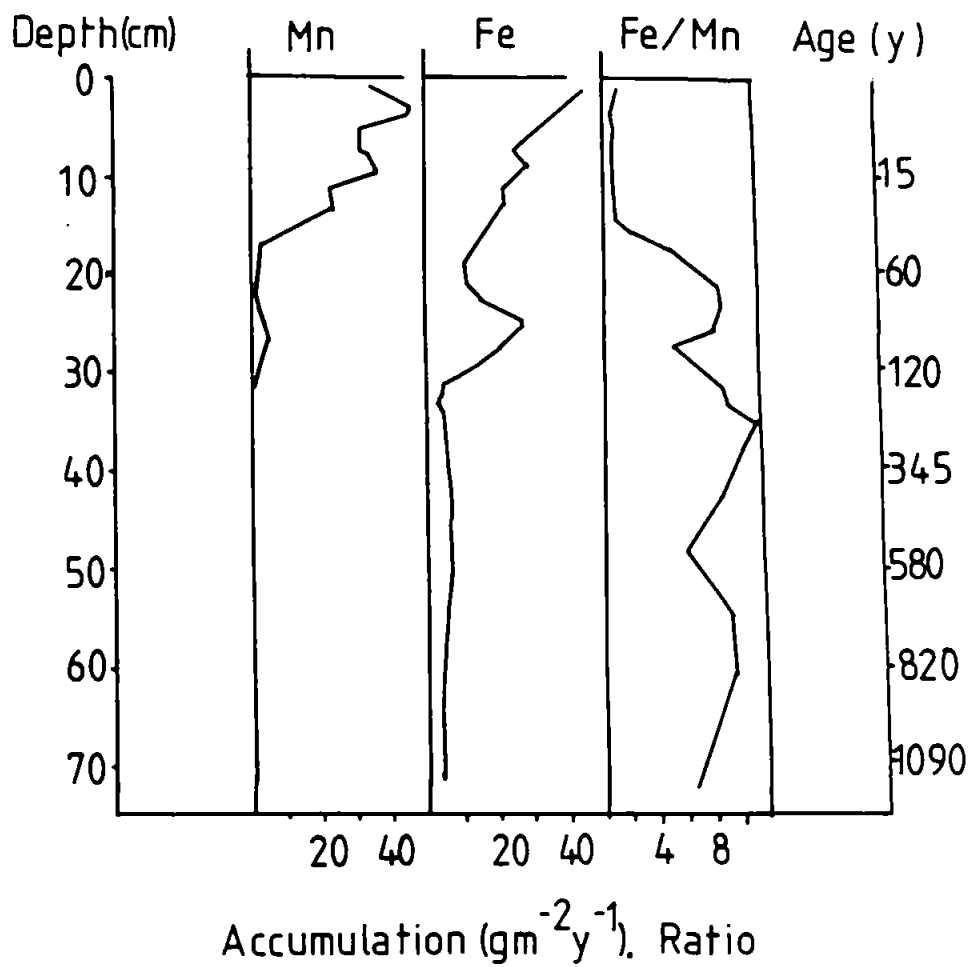
Figure 19. Profiles of manganese, iron and the iron :
manganese ratio from Harvey's Lake as
accumulation rate. Age in years before 1981
(from Engstrom et al., 1985).

oxygen stress during the summer months (Section 2.2), which may have been of longer duration in the past when the lake was deeper. If the Pool had seasonally-reducing conditions at the sediment-water interface then the Fe:Mn ratio of the sediment would be predicted to increase during periods of anoxia. This is because manganese would be dissolved preferentially to iron. At overturn when the bottom-waters are reoxygenated the Fe:Mn ratio in the sediment would be lowered because under oxidising conditions both manganese and iron would be deposited. The analysis of iron and manganese could, therefore, be important in identifying the palaeo-redox conditions of Loe Pool.

3.4.3 Sodium, Potassium, Calcium and Magnesium

The concentrations of alkali and alkaline earth metals in sediments are principally a function of supply. Mackereth (1966) found from sediments of three lakes in the English Lake District that magnesium, calcium and potassium were associated with the mineral products of erosion. Many other workers have subsequently related high sedimentary concentrations of magnesium, sodium and potassium to high levels of erosion from the catchment (Renberg, 1976; Huttunen & Tolonen, 1977; Huttunen, Merailäinen & Tolonen, 1978; Rowlatt, 1980; Pennington, 1981; Engstrom, 1983)

It should be noted that both calcium and magnesium are readily solubilised and hence are liable to be leached from land. In sediment from Esthwaite Water, Mackereth (1966) found elevated concentrations of calcium in coarsely laminated clays. These were

known to be of glacial origin. In more recent sediments the calcium concentration was lower and perhaps associated with organic matter. Mackereth concluded that the calcium concentration in sediment only increased when erosion within the catchment is high enough to prevent prior removal by leaching.

Ochsenbein et al. (1983) related the concentration of magnesium in lake sediment to erosion rather than leaching. Magnesium was positively correlated with the mineral chlorite and also with aluminium, which is not readily leached.

Analysis of the seasonal concentrations of sodium, calcium and magnesium in lake water by Sutcliffe et al. (1982) revealed considerable variations. Sodium and potassium had higher concentrations in winter; the high sodium levels being attributed to input from the increased seasonal rainfall. The concentrations of calcium and magnesium in lake water were greatest in the summer and least in the winter months. The high summer values were thought to be caused by low rainfall preventing dilution, high evaporation so further concentrating the calcium and magnesium and to the biological production of calcium in the lake epilimnion.

At Loe Pool, there is a clear peak input of streamflow and minerogenic matter in the winter months. This may be reflected in the concentration of the alkali and alkaline earth metals in the seasonal laminations.

3.4.4 Zinc, Copper, Nickel, Cobalt and Lead

The concentration of heavy metals in lake sediment is a function of supply from the catchment and limnological conditions

controlling precipitation to the sediment. Mackereth (1966) gives the concentrations of cobalt, nickel, copper and zinc (Table 7) in lake sediment and bedrock. He noted that the ratio of the concentrations of elements in lake sediment:lake water was approximately 40,000:1 for zinc, 64,000:1 for copper and 100,000:1 for cobalt. Clearly mechanisms for the precipitation of these elements to the sediment are important.

In Esthwaite Water, a lake essentially unpolluted with respect to heavy metals, Mackereth (1966) noted that co-precipitation of zinc, copper and cobalt with iron and manganese is a possible controlling factor. Cobalt appears to be associated with iron and copper with manganese.

In contrast to Estwaite Water, the sediment formed in Loe Pool has been heavily polluted by various heavy metals as a result of the mining which has occurred within the catchment of the lake. This pollution input will probably be an important source of metals within the sediment profile. Yim (1981) found that tin mine tailings in Cornwall contain higher concentrations of tin, copper, zinc, iron, manganese, arsenic and tungsten than the crustal average. Perhaps Loe Pool can be visualised as a large tailings lake during times of heavy mine working within the catchment.

Potential reasons for differing concentrations of heavy metals between the seasonal laminations formed in Loe Pool may be one or a combination of:

1) a function of concentration or dilution by input of mine waste

2) seasonal variations in streamflow and erosion of terrestrial material

3) co-precipitation with other elements whose levels are

Sediment	Co	Ni	Cu	Zn
Windermere South Basin	20	55	32	200
Esthwaite	35	50	30	200
Ennerdale	18	18	16	140
Lithospheric Average	23	80	70	132

Table 7. Mean Concentration (ppm) of Zinc, Copper, Nickel and Cobalt from 3 English Lakes' Sediment together with the Lithospheric Average
(Source, Mackereth, 1966).

controlled by redox conditions at the sediment-water interface.

3.5 Carbon and Nitrogen

The organic fraction of lake sediment has been widely studied in palaeolimnological research (Renberg, 1978a; Renberg, 1978b; Eglinton & Barnes, 1978; Rea, Bourbonniere & Meyers, 1980; Pennington & Lishman, 1984, Alberts & Dickson, 1985). Some workers have assessed the organic fraction by the figure for loss on ignition (Gorham & Sanger, 1976; Hickman, 1981; Hilton & Gibbs, 1984). This may well be an overestimate owing to losses of some non-organic compounds. Other workers have assessed both carbon and nitrogen concentrations using an elemental analyser (Tipping, Woof & Cooke, 1981; Oschenbein et al., 1983; Hamilton-Taylor, Willis & Reynolds, 1984; Tipping, Thompson & Davison, 1984). This technique analyses total carbon which includes both organic carbon and inorganic carbonate fractions. It is possible to examine the organic carbon component by pre-fuming the sediment fraction with concentrated HCl to remove the carbonate (Rea et al., 1980; Hedges & Stern, 1984). The difference between total carbon and organic carbon concentrations obtained by elemental analysis is the inorganic carbon or carbonate fraction. The carbonate content will be reviewed in section 3.7.

Organic carbon and nitrogen values have been widely used in palaeolimnological research (Pennington et al., 1977; Hamilton-Taylor et al., 1984; Pennington & Lishman, 1984). Meyers et al., (1984) noted that the production and

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destruction of organic matter within natural water bodies are dynamic processes. These are related to a number of environmental factors. For example, the availability of sunlight and dissolved nutrients, the water temperature and the composition of aquatic biological communities. It is known that only a small percentage of organic material escapes remineralisation whilst sinking to the sediment (Wakeham, Schaffner & Giger, 1980; Dean, 1981). Once incorporated into the sediment further degradation can occur by microbial action (Giger, Schaffner & Wakeham, 1980).

The preservation of organic matter is influenced by the redox conditions at the sediment-water interface, and the sedimentation rate. Generally an anoxic sediment with a high rate of sedimentation to it will have greater preservation of organic matter than a site with oxic waters and a lower sedimentation rate (McEvoy, 1983). For these reasons sedimentary carbon and nitrogen values can only give a guide to the former levels of production or sources of organic matter within water-bodies. More specific information is found by the analysis of biomarkers such as organic geolipids (Barnes & Barnes, 1978; Brassell, 1980; Brassell et al, 1980a; Brassell et al, 1980b; Brassell et al, 1980c; Cranwell, 1980; Brassell et al, 1981; Cranwell, 1981 ; Cranwell, 1982) and pigments (Brown, 1969; Gorham & Sanger, 1976; Swain, 1985).

Trends in the Carbon:Nitrogen (C:N) ratio can be used to provide information on the source of organic matter. According to Dean (1981) allochthonous organic debris tends to be depleted in compounds containing nitrogen and enriched in those consisting largely of carbon. Hence the C:N ratio of material with a

terrestrial origin can be quite high. Müller (1977) suggested that land-derived organic debris can typically have C:N ratios of 12-14. In contrast, Müller found C:N ratios of around 6.0 in marine plankton.

The C:N ratio has the potential for distinguishing material produced from the terrestrial or aquatic system in the laminated sediment formed in Loe Pool.

3.6 Humic Substances

The organic matter in lake sediments is composed of many different fractions, for example, pigments and hydrocarbons. One fraction of particular significance is the humic substances. Humic material forms 9% to 80% of the total organic carbon in lake sediment (Ishiwatari, 1971; Kemp & Johnston, 1979; Ishiwatari, Ogura & Horie, 1980; Nriagu & Coker, 1980; Alberts & Dickson, 1985). Humic substances are amorphous, black or brown, hydrophilic, acidic substances with large molecular weights (Schnitzer & Khan, 1972; Choudhry, 1984). They may be subdivided into three categories:

Fulvic acids: soluble in acid and base.

Humic acids: soluble in dilute alkali but precipitated by acid.

Humin: insoluble in dilute acid or base and remain bound to organics.

Humic substances are mainly composed of carbon and hydrogen, but also contain nitrogen, sulphur and oxygen. They may be of terrestrial or marine origin (Choudhry, 1984). Work by Tipping &

Woof (1983a & 1983b) found increased concentrations of humic substances in the anoxic hypolimnion of Esthwaite Water. These elevated concentrations were correlated with increases in the concentration of iron. They suggested that humic substances accumulating in the hypolimnion are produced by anaerobic decomposition of settled particulate matter (mostly dead algae). This was for two reasons. Firstly because no close correlation with iron would be expected. Secondly, because the humic substances themselves would probably have different characteristics from those of terrestrial origin deposited under the oxic epilimnion.

The importance of this to the accumulation of humic substances in the summer and winter laminations of Loe Pool is that more humic substances of terrestrial origin may be transported to the lake during the winter months when run-off from the catchment is highest. However the proportion of these humic substances that are preserved in the sediment depends on the lake-redox conditions. A greater proportion of humic matter may be preserved if deposited under anoxic than oxic bottom waters.

3.7 Carbonate

According to Dean (1981) the four most important components in the sediments of modern north temperate lakes are detrital clastic material, biogenic silica, carbonate minerals and organic matter. The quantities and concentrations of carbonate within lake sediment are influenced by many factors. These are summarised in reviews by Kelts and Hsü (1978) and Dean (1981). This introduction does not

present all of this information, but briefly summarises the salient points.

The most common carbonate present in lacustrine sediment is calcium carbonate (calcite, $CaCO_3$). Others precipitated include magnesium carbonate (dolomite,$CaMgCO_3$), aragonite ($CaCO_3$) and siderite ($FeCO_3$).

The concentration of carbonate formed in lake sediment is a function of the amount of that mineral precipitated to, and preserved, in the sediment, together with the amount of other components (chiefly, clastic material, biogenic silica and organic matter). The concentration of carbonate will vary if any of these major components change.

The amount of carbonate clastics that form are produced by a combination of four processes (Kelts & Hsü, 1978):

1)   Input from the erosion and transport of
      allochthonous carbonates.

2)   Production of calcareous skeletons, structural
      parts and internal waste products within living
      organisms.

3)   Primary inorganic precipitation and sedimentation
      of carbonate minerals.

4)   Post depositional changes or early diagenetic
      reactions.

The mechanism which dominates varies both between lakes and within lakes.

Calcareous varves have been reported in many lacustrine sediments (Thompson & Kelts, 1974; Ludlam, 1979; Haworth, 1980; Peglar et al., 1984). For example at Diss Mere, Norfolk, a series of

annually-laminated calcite-rich sediments have been reported (Peglar et al., 1984). Diss Mere is a small (c. 3 ha) hard-water lake with 17m of organic sediments. The authors described varves consisting of dark and light couplets. A section of the laminated sediment was examined by energy-dispersive X-ray microanalysis. The pale laminae were reported to contain mainly calcium carbonate and the dark laminations iron, silica and sulphur compounds with organic matter. Analysis of sedimentary pollen, diatom remains and chrysophycean cysts suggested that the pale sediment was deposited in the late spring and early summer and the darker sediment in the late summer, autumn and winter. The authors concluded that the seasonal supply of calcite was the major factor in the formation of the varves.

Peglar et al. (1984) suggested two possible reasons for the precipitation of carbonate, 1) photosynthetic removal of carbon dioxide and 2) increased water temperature. The photosynthetic removal of carbon dioxide is well documented to be a major cause of carbonate precipitation in hard-water lakes (Wetzel, 1960; Megard, 1967; Megard, 1968; Müller, 1970; Otsuki & Wetzel, 1974; Müller & Wagner, 1978). This assimilation of carbon dioxide follows the reaction:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$
$$CO_3^{2-} + Ca^{2+} \rightleftharpoons CaCO_3$$
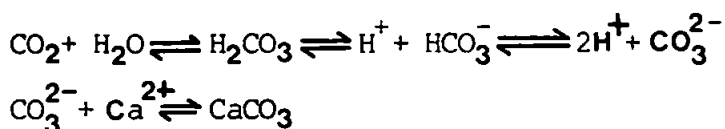
The second possible cause of calcite precipitation is the increase in water temperature. This changes the dissociation constant of carbonic acid which subsequently raises the concentration of calcium carbonate until supersaturation and deposition occurs. Such reactions are dependent on the pH of the lake water. The

solubility and forms of dissolved inorganic carbon according to pH in hard-water lakes are illustrated (Fig. 20).

Peglar et al. (1984) did not propose either of these reasons as the actual controlling mechanism for the seasonal deposition of calcite in Diss Mere sediment, but suggested that further work was needed to understand the processes of carbonate precipitation and dissolution.

A further factor which has been reported as influencing carbonate precipitation is the redox condition of the aqueous system (Degans & Stoffers, 1976). The authors investigated several stratified water bodies from numerous environments over a period of more than 10 years. They concluded that in oxic conditions, calcite may be precipitated but that if the bottom water was anoxic, then the mineral would be redissolved prior to or just after deposition. If the nutrient rich anoxic waters are oxygenated, for example at overturn, then primary productivity will be stimulated and carbonates may be precipitated to the sediment.

Many workers have analysed carbonate in lake water and sediment and produced results of palaeolimnological significance. Of particular interest to the Loe Pool study are changes in the seasonal supply of carbonate.

Hilton and Gibbs (1984/85) analysed carbonate from surface sediment in Esthwaite Water. They found significantly higher values in January than August. This may be caused by seasonal variations in rainfall and hence supply of material from the catchment to the lake. In winter, allochthonous input and precipitation of calcite are high. In contrast, in the summer, the input of allochthonous calcite is at a minimum, so calcite precipitation is proportionally
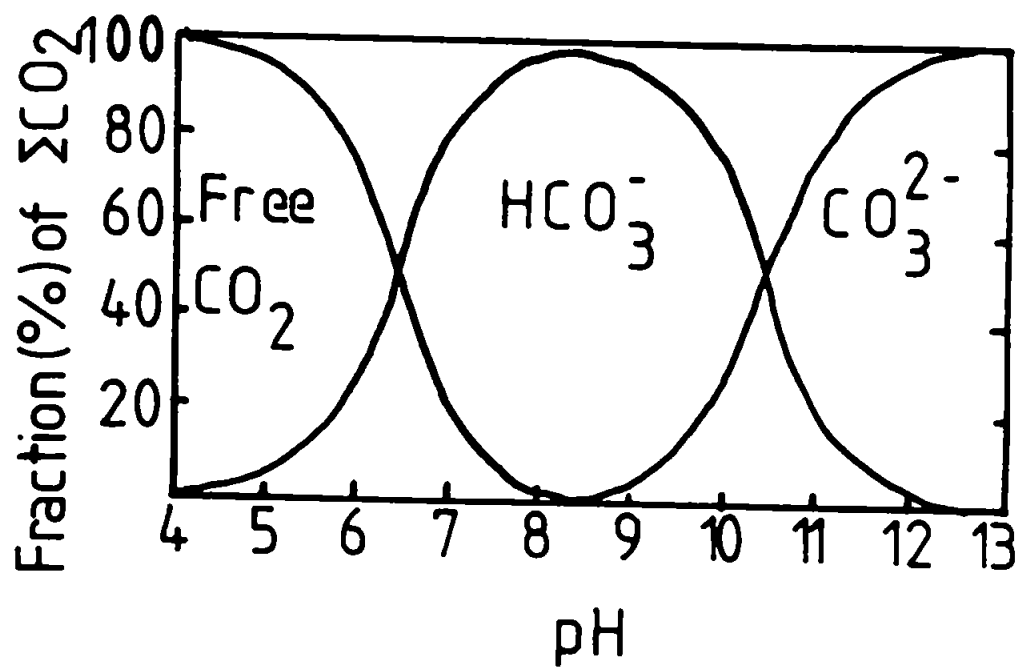
Figure 20. Distribution of relative abundances of dissolved CO_2, HCO_3^- and CO_3^{-2} in water at 1 atmosphere as a function of pH (source Dean, 1981).

lower.

Although not an analysis of seasonal variations, Rea et al. (1980), in a study of sediment from the Great Lakes, found variations in carbonate concentrations between rapidly accumulating sediment and sediment with a more "normal" deposition rate. In a layer of rapidly accumulated sediment there were greater concentrations of carbonate and inorganic carbon and lower concentrations of organic carbon. In the organic fraction a greater proportion of humin and less fulvic acid were present. The authors suggested that the more rapid burial of sediment retards the dissolution of carbonate. Perhaps this enhanced concentration caused by rapid burial would occur in a winter season when there is more material supplied from the catchment and so more rapid burial of sediment.

The carbonate composition of the seasonal laminations formed in Loe Pool will be a function of supply from the catchment, and limnological conditions controlling precipitation and dissolution. If these factors vary on a seasonal basis then there is potential for variation of the carbonate concentration in the seasonal laminations deposited.

3.8 Introduction to Pigments

The most common light harvesting pigments found in aquatic plants, animals and sediments are the chlorophylls and carotenoids (Orr & Grady, 1957; Orr, Emery & Grady, 1958).

3.8.1.1 Chlorophylls and their Degradation Products

The major chlorophyll is chlorophyll a, a tetrapyrrole nucleus joined in a complex called a porphyrin. Chlorophyll is a magnesium chelate of the porphyrin, esterified with the long chain alcohol, phytol. Structures of selected chlorophylls and their degradation products are shown (Fig. 21). The replacement of the magnesium chelate by hydrogen results in phaeophytin. The substitution of the phytol side chain by hydrogen forms the chlorophyllide derivative. Phaeophorbide has both the magnesium chelate and the phytol side chain replaced by hydrogen. A further derivative of the chlorophyll and chlorophyllide molecules is the allomer product, the allomer of chlorophyll a being designated chlorophyll a'. Allomerisation is the oxidation of the carbon in the 10 position of the cyclopentane ring resulting in the removal of the carbon 10 proton (Katz et al., 1968).

3.8.1.2 Carotenoids

The carotenoids are isoprenoid, polyene structures which include the yellow/brown pigments of carotenes and xanthophylls (Swain, 1970).The carotenes are hydrocarbons and the xanthophylls additionally contain oxygen. As well as aiding photosynthesis, carotenoids function in photoprotection of bacterial, algae, fungi and higher green plants and possibly in phototropism and phototaxis (Burnett, 1976). Carotenoids appear to be synthesised by higher plants, spore-bearing vascular plants, algae and photosynthetic

chlorophyll <u>a</u>	R = phytyl
phaeophytin <u>a</u>	R = phytyl, Mg replaced by H
chlorophyllide <u>a</u>	R = H
phaeophorbide <u>a</u>	R = H, Mg replaced by H
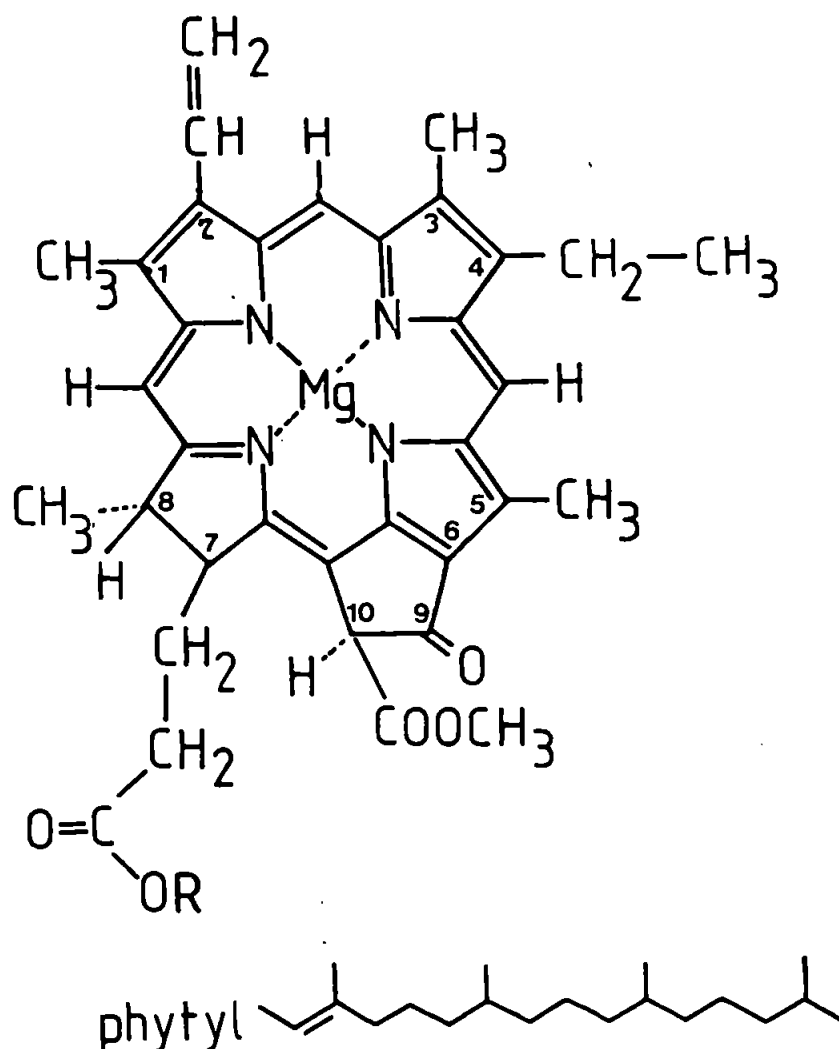
Figure 21. Structure of chlorophyll <u>a</u> and selected degradation products (cont.).
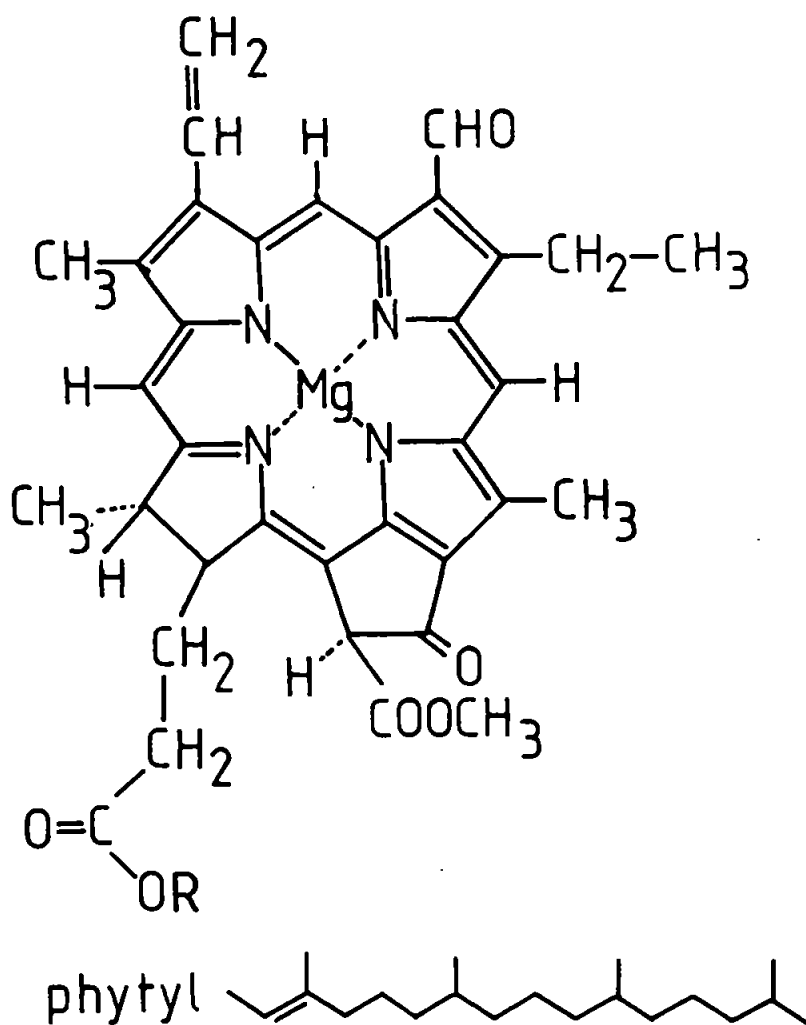
chlorophyll __b__	R = phytyl
phaeophytin __b__	R = phytyl, Mg replaced by H
chlorophyllide __b__	R = H
phaeophorbide __b__	R = H, Mg replaced by H

Figure 21 (cont.). Structure of chlorophyll __b__ and selected degradation products (cont.).
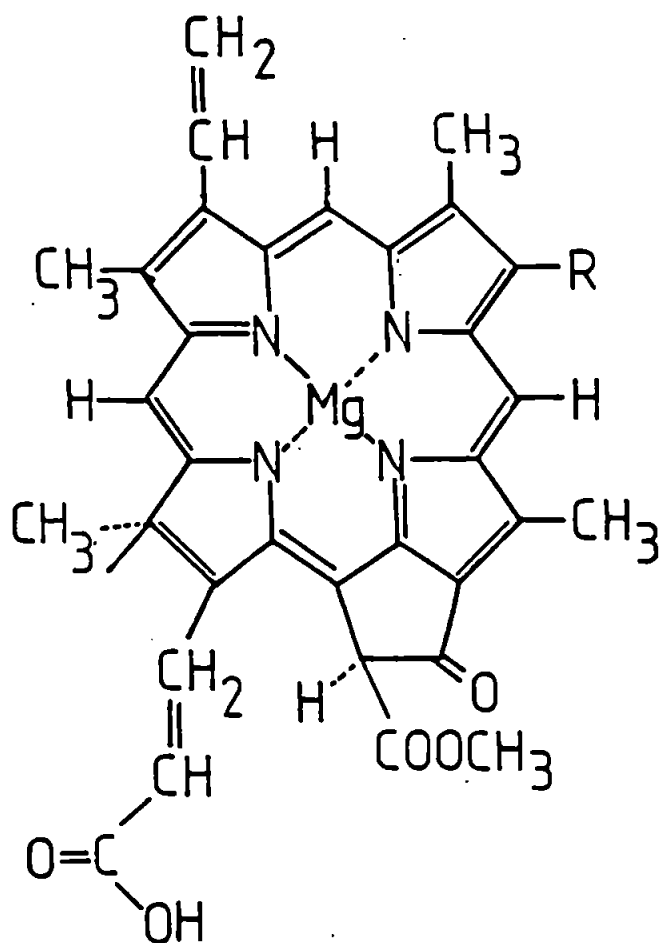
chlorophyll c 1 $R = CH_2-CH_3$

chlorophyll c 2 $R = CH = CH_2$

phaeophytin c 1 $R = CH_2-CH_3$, Mg replaced by H

phaeophytin c 2 $R = CH = CH_2$, Mg replaced by H

Figure 21 (cont.). Structure of chlorophyll c_1 and c_2 and selected degradation products.

bacteria (Goodwin, 1976). Structures of selected carotenoids are illustrated (Fig. 22).

3.8.2 Occurrence of Pigments in Terrestrial and Aquatic Organisms

3.8.2.1 Chlorophylls

Chlorophyll a is widely distributed amongst oxygen-evolving photosynthetic organisms (Table 8). This prevents the use of chlorophyll a as a specific source indicator. Chlorophyll b exists in chlorophytes and higher terrestrial plants and chlorophyll c occurs mainly in diatoms. If it is assumed that the majority of chlorophyll b has a higher plant origin it may be possible to use the chlorophyll b:chlorophyll c ratio to deduce whether the likely source of the pigments is terrestrial or aquatic.

3.8.2.2 Carotenoids

The carotenoids are as widely distributed as the chlorophylls. The leaves of all green plants contain the major carotenoids, b-carotene, lutein, violaxanthin and neoaxathin. Other carotenoids that may occur in higher plants include a-carotene, b-cryptoxanthin, zeaxanthin and antheraxanthin (Goodwin, 1976). Carotenoids occur in all algae. The distribution of selected examples are shown in Table 9. The carotenoids have great structural specificity, particularly in the lower plants. This

- 82 -
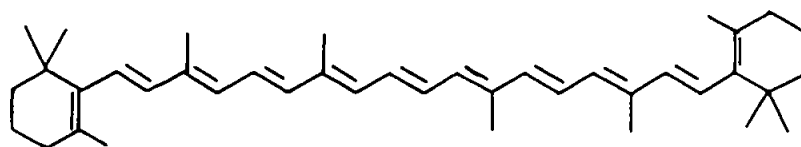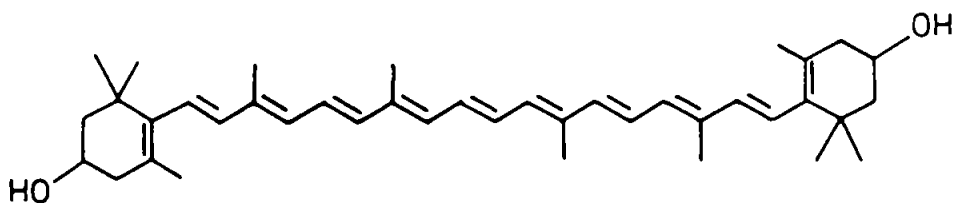
b-Carotene

Zeaxanthin
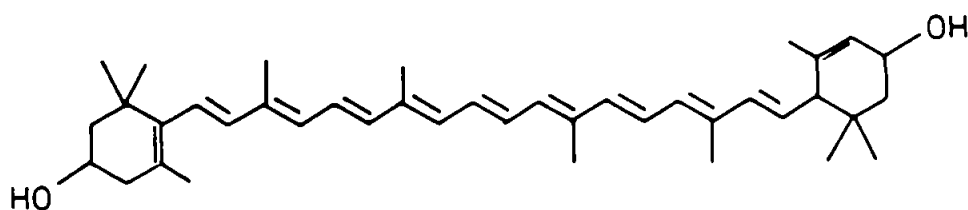
Lutein
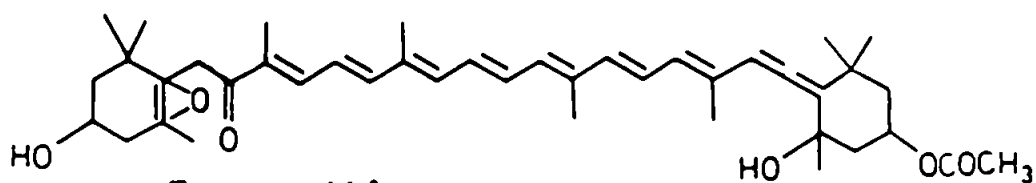
Fucoxanthin
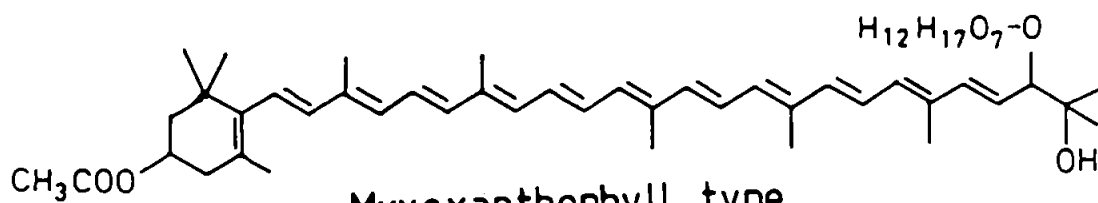
Myxoxanthophyll type
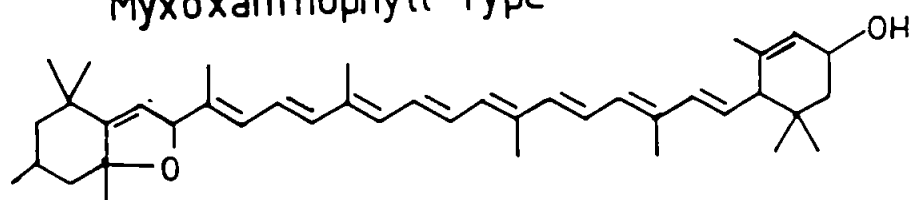
Lutein 5, 8-epoxide

Figure 22. Structures of selected carotenoids.

Group	Chlorophyll		
	a	b	c
Vascular plants	*	*	
Bryophyta	*	*	
Algal division:			
Cyanophyta	*		
Rhodophyta	*		
Cryptophyta	*		*
Pyrrophyta	*		*
Bacillariophyta	*		*
Phaeophyta	*		*
Chrysophyta	*		*
Xanthophyta	*		
Euglenophyta	*	*	
Chlorophyta	*	*	

* = present

Table 8. Chlorophyll distribution in oxygen-evolving
photosynthetic organisms
(Source, Allen, 1966).

Algal Class	Major Carotenoids
Chlorophyceae	β-carotene, lutein and neoxanthin
Rhodophyceae	α- and β-carotene lutein and zeaxanthin
Xanthophyceae and Eustigmatophyceae	β-carotene, diadinoxanthin, diatoxanthin and heteroxanthin
Chrysophyceae and Haptophyceae	Fucoxanthin, diatoxanthin and diadinoxanthin
Phaeophyceae	β-carotene, violaxanthin and fucoxanthin
Bacillariophyceae	β-carotene, diatoxanthin, diadinoxanthin and fucoxanthin
Pyrrophyceae	Peridinin
Cryptophyceae	α-carotene, alloxanthin, crocoxanthin and monadoxanthin
Euglenophyceae	β-carotene, zeaxanthin, neoxanthin and diadinoxanthin
Cyanophyceae	β-carotene, echinenone, zeaxanthin and myxoxanthophyll

Table 9. The Major Carotenoids of the Algae
(Source, Watts, 1975).

allows their use as chemosystematic markers (Liaaen-Jensen, 1977).

3.8.3 Techniques of Analysis

Classical quantitative methods involve extraction by an organic solvent followed by spectrophotometric analysis (Strickland & Parsons, 1972). Quantification is achieved by noting absorbance at certain wavelengths and inserting these values in set equations.

A review by Mantoura and Llewellyn (1983) describes numerous problems associated with the classical techniques of pigment analysis. These include overlap of pigment emission and absorption bands giving spurious values, poor quantitative distinction between chlorophylls and their degradation products, a range of equations for the same pigment which may give different results and inability to determine the concentration of individual carotenoids. If algal mass is to be predicted from sedimentary pigments, then Jacobsen (1978) suggests that errors of up to 400% can occur.

Problems of poor quantification and lack of separation between pigments can be overcome by certain advanced chromatographic techniques. Rapid and accurate measurement of pigments is routinely performed using high pressure liquid chromatography (H.P.L.C.) coupled with fluorescence or absorbance detectors (Mantoura & Llewellyn, 1983; Sartory, 1985).

3.8.4 Application of Pigment Studies in Palaeolimnology

The presence of pigments in lake sediment has been known for some time (Vallentyne, 1957). Sedimentary pigments have been investigated from many sites (Gorham, 1960; Fogg & Belcher, 1961; Brown, 1968; Gorham et al., 1974; Gorham & Sanger, 1975; Handa, 1975; Gorham & Sanger, 1976; Rawlence, 1984). Pigments have been used to determine lake production and trophic status. For example, analysis of surface sediment from five lakes has shown that the concentration of chlorophylls and their degradation products vary with the level of productivity (Gorham, 1960). This work was extended to a study of nineteen English lakes, where a close correlation between algal standing crop, chlorophyll content of the epilimnion and sedimentary pigments was found (Gorham et al., 1974). This qualitative relationship between trophic status and sedimentary pigment content is reviewed in the literature (Brown, 1969; Barnes & Barnes, 1978).

Such a relationship between trophic status and sedimentary pigment concentration has been found in Shagawa Lake, North Eastern Minnesota. Shagawa lake has had a similar recent history to Loe Pool (Bradbury & Megard, 1972; Bradbury & Waddington, 1973; Gorham & Sanger, 1976; Simola et al., 1981). The area around the lake was cleared by logging in the 1870's. Since that time, mining and the development of tourism have occurred in the lake's catchment. These changes have resulted in high concentrations of haematite being deposited, increased influx of cladoceran and

diatoms and a greater phosphorus loading (Gorham & Sanger, 1976). Gorham & Sanger (1976) examined concentrations of chlorophyll derivatives and carotenoids in Shagawa Lake sediment. They found that concentrations in recent sediment (1 to 10 cm deep) were three times higher than in the organic matter of sediment from the presettlement period (34 to 149 cm deep) which is illustrated in Figure 23. The authors suggested that sedimentary pigments are a more sensitive indicator of eutrophication than are diatoms and cladocera. However, if quantitative as well as qualitative data are required, then individual chlorophyll and carotenoid pigments must be analysed.

The isolation of pigments specific to certain classes of plant, for example, algae, allow a more precise interpretation of a lake's history. Züllig (1961) separated the carotenoid, myxoxanthophyll, from the sediment of five Swiss lakes. He found from quantitative measurements of the pigment a record of relative abundance of the algae from the time of their first appearance to the present. Oscillaxathin, a carotenoid specific to the blue-green alga Oscillatoria, has been isolated from lake sediment (Brown & Colman, 1963; Griffiths, Perrott & Edmondson, 1969). Griffiths & Edmondson, (1975) reported the occurrence of oscillaxanthin in the sediments of Lake Washington. They correlated the vertical distribution of the pigment in the sediment with eutrophication and the subsequent increase of algal populations since 1955.

Engstrom, Swain & Kingston (1985) examined a core from Harvey's Lake, Vermont, for metal and pigment concentrations and diatom frequencies. Harvey's Lake is a moderately productive, deep (44m) and clear lake. It was dominated by a population of the blue-green
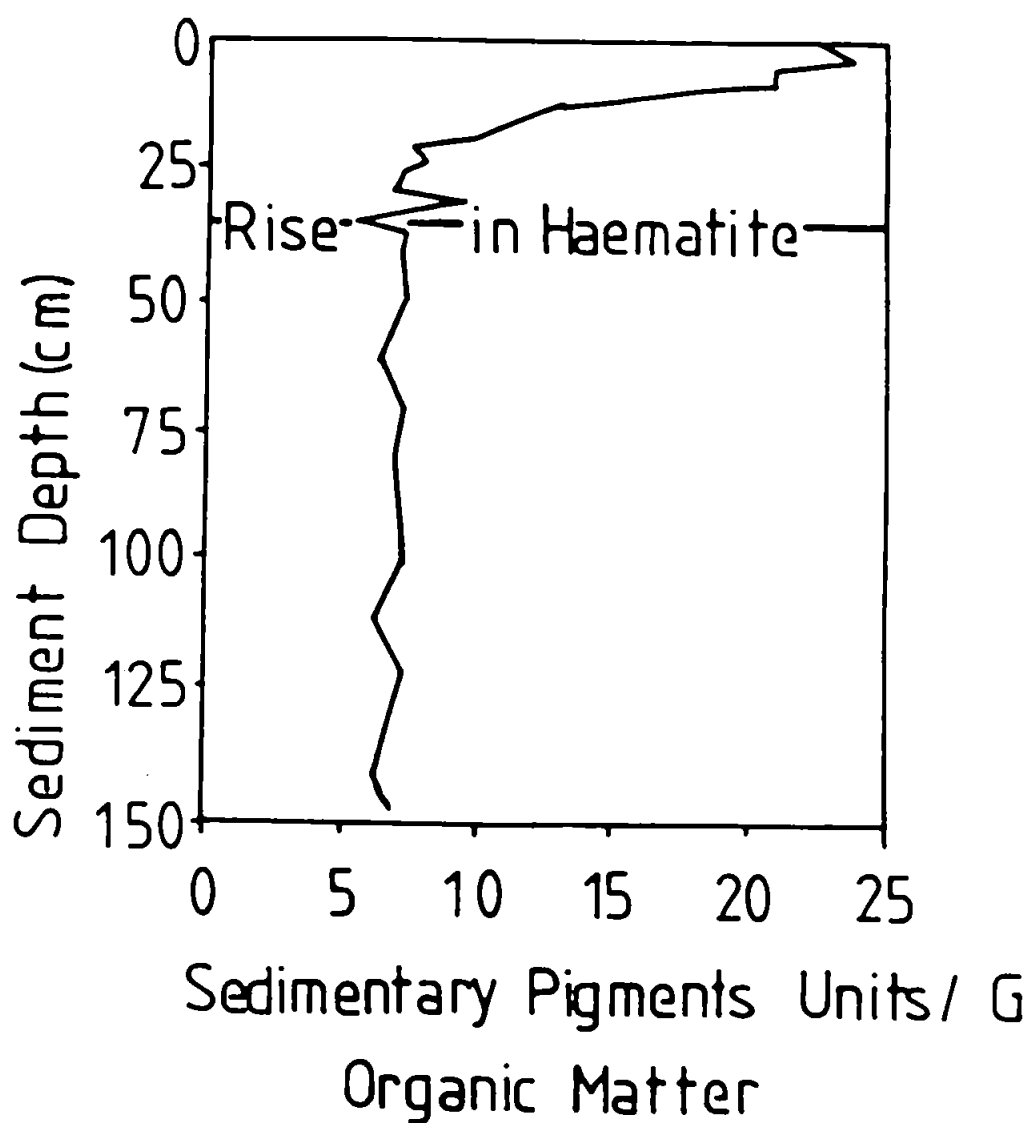
Figure 23. Preservation of chlorophyll derivatives in sediment
from Shagawa Lake in north eastern Minnesota
(from Gorham and Sanger, 1976).

algae, _Oscillatoria_ _rubescens_ (Engstrom et al., 1985). The carotenoid fraction was partitioned from the chlorophylls and analysed with a spectrophotometer. The sedimentary pigments myxoxanthophyll and oscillaxanthin, which are unique to blue green algae, were quantified (Fig. 24). Results showed that a greater accumulation of sedimentary pigments occurred after settlement in 1780 and again after 1945. The authors attributed this to increased levels of primary production.

Many other palaeolimnological investigations have revealed valuable information from the analysis of sedimentary pigments (Gorham & Sanger, 1975; Daley, Brown & McNeely, 1977; Sanger & Crowl, 1979; Züllig, 1982; Guilizzoni, Bonomi & Ruggin, 1983).

Great care must be taken with the extraction and analysis of pigments because of their lability. Throughout the processes of transport to, or production in the lake, precipitation to the sediment and subsequent burial, many factors can influence the final form of any pigment. Daley and Brown (1973) reported destruction of the tetrapyrrole ring by photochemical action in chlorophyll from senescent cultures of green and blue-green algae. In one culture chlorophyll a was destroyed more readily than chlorophyll b. This result questions the validity of the use in palaeolimnology of chlorophyll b:chlorophyll c ratios. Daley (1973) found that chlorophyll incubated with a bacteria and a virus was only destroyed in the presence of light. Daley concluded that photodegradation was important in the destruction of pigments and that following burial chlorophyll may not be degraded at the same rate as other organic matter.

Chlorophyll may be destroyed by zooplankton as well as light.

Oscillaxanthin Myxoxanthophyll

Depth
(c m)

Age
(y)

Accumulation
(units dm^{-2}y^{-1})
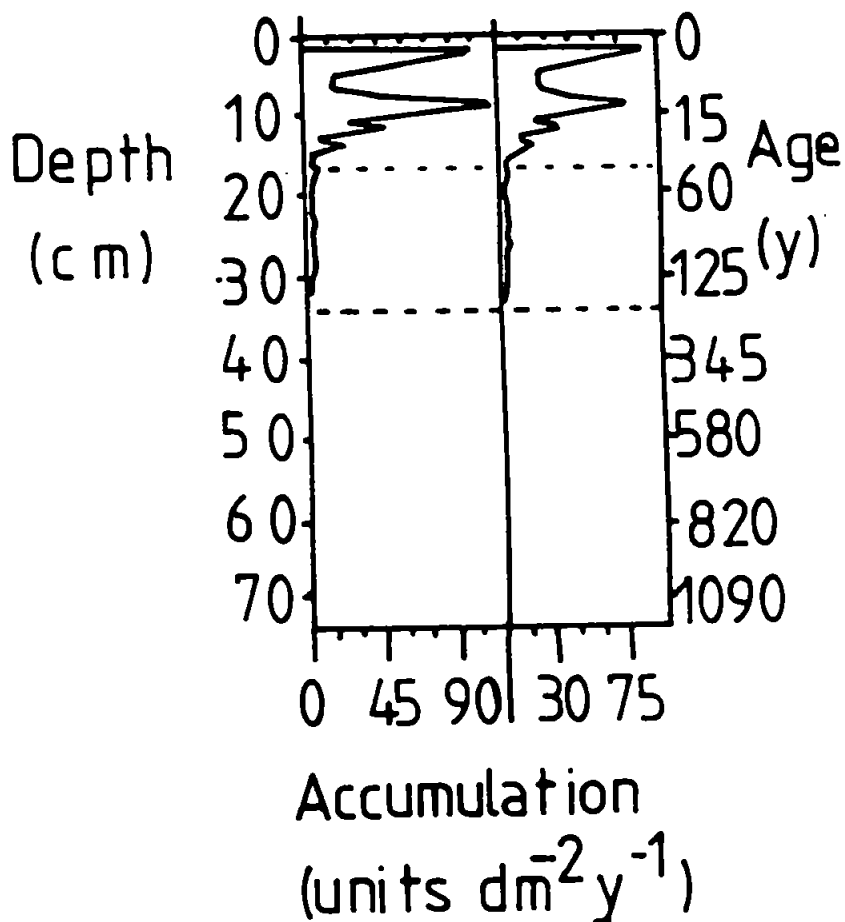
Figure 24. Oscillaxanthin and myxoxanthophyll in a core from
Harvey's Lake, units are µs
(from Engstrom et al., 1985).

Currie (1962) noted that a herbivore <u>Calanus</u> <u>finmarchicus</u> would eat plankton rich in chlorophyll <u>a</u>, but would excrete in faecal pellets a chlorophyll degradation product. Daley (1973) fed the green alga <u>Scenedesmus</u> <u>quadricauda</u> and the blue-green <u>Anacystis</u> <u>nidulans</u> to the cladoceran <u>Daphnia</u> <u>pulex</u>. Chlorophyll was reported to be readily destroyed, and the phaeophytins and to a lesser extent, phaeophorbides accumulated in the faeces. The authors suggested that the presence of phaeophytins in lake sediment is an indicator of zooplankton grazing.

Chlorophyll may be degraded by oxygen in the lake water. Santelmann (1981) noted that pigment concentrations in shallow, non-stratifying eutrophic lakes can be as low as in oligotrophic lakes and in meromictic oligotrophic lakes, the concentrations may be as high as in eutrophic lakes. Santelmann concluded that the profundal oxygen concentration plays an important role in the destruction or preservation of chlorophyll. Where there are reducing conditions, then pigments are more likely to be preserved. This in turn implies that limnological properties must be considered when interpreting sedimentary pigment concentrations.

Analysis of chlorophylls <u>a</u> and <u>b</u>, and pheophytins <u>a</u> and <u>b</u> from recent sediment deposited in Priest Pot, Cumbria by Keely and Brereton (1986), has shown that concentrations and ratios of pigments change after deposition. Following quantitative analysis the authors found that there was a steady decrease in the sediment profile of the ratios of chlorophylls to pheophytins (Table 10). When interpreting sedimentary pigments some authors use ratios of one pigment to another (Gorham <u>et al.</u>, 1974; Gorham & Sanger, 1976; Engstrom <u>et al.</u>, 1985). It must be concluded that such

Depth (cm)	Chlorophyll a:Phaeophytin a
0-5	0.3
10-15	0.25
20-25	0.128
30-35	0.114
40-45	0.077
50-55	0.114
60-65	0.092
70-75	0.078
80-85	0.079

Table 10. Ratio of Chlorophyll a to Phaeophytin a
with Depth
(Source, Keely and Brereton, 1986).

measures or ratios must be used with care because of differential degradation rates between the pigments being considered.

Engstrom et al. (1985) suggested that accumulation rates rather than sedimentary pigment concentration may be a better indication of lake trophic status. An increase or decrease in sedimentary content is not necessarily an indication of changing lake trophic status. An increase in sedimentary pigment concentration may indicate greater primary production.

The use of accumulation rates must also be treated with care. Pigment concentrations may be changed by variations in the supply of material from the catchment. In addition, the phenomenon of sediment-focussing may cause variation in sediment accumulation rates with time (Davis & Ford, 1982). Pigment accumulation rates from sediment cored in different parts of the lake may also be an inappropriate measure of trophic status. This is because limnological conditions which vary across a lake bed (for example dissolved oxygen concentration and light penetration) may influence the degree of pigment degradation.

The techniques of pigment analysis have the potential for revealing firstly, whether each lamination had a predominantly terrestrial or aquatic source and secondly, the likely season in which each lamination was deposited, in the varved sediment formed in Loe Pool.

3.9 Selected Organic Geochemical Properties of Sediment

3.9.1 Introduction

The organic matter within freshwater sediment consists of detritus derived from terrestrial and aquatic biota, modified by chemical and biological (chiefly microbial) action both before and after deposition in sediment (Cranwell, 1980). The terrestrial fraction is termed allochthonous and includes higher plant material. The organic component may be transported over considerable distances prior to deposition in the lake and hence this may be modified by chemical or biological action. The autochthonous fraction is that matter produced within the lake which includes lower plant material, for example, algal remains. This fraction is also liable to alteration prior to deposition. Once sedimented, organic substances with both autochthonous and allochthonous origins may be degraded.

The initial process of degradation within the sediment is diagenesis. This is the chemical and/or biochemical (microbial) alteration of organic matter (Simoneit, 1978). Products of diagenesis are termed the in situ fraction, or where they result specifically from microbial action, the bacterial component. Didyk et al. (1978) note that diagenesis both depends upon and influences the depositional environment. The redox environment may be moderated by the oxygen demand of decaying matter. In addition, different degradation pathways may be followed by

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compounds deposited under oxic or anoxic conditions. The authors conclude that redox potential and acidity are important factors in the degradation or preservation of organic matter.

Organic geochemical analysis of the extractable lipid fraction of lake sediments have shown a complex mixture of organic compounds (Cranwell, 1975; Barnes & Barnes, 1978; Cranwell, 1982). Some of these types of compounds have been used as indicators of lipid source, whether autochthonous (Cardoso et al. 1983), allochthonous (Cranwell, 1976; Cranwell, 1977a; Brassell, 1980), or produced by diagenesis (Didyk et al., 1978; Brassell et al., 1981). Compounds produced in situ may indicate the likely redox conditions at the time of sediment deposition or the level of microbial activity (Perry et al., 1979; Louda & Baker,1984;).

Initially some features of a lipid extract are examined. The occurrence of lipids within sediment will be reviewed with the aim to differentiate between their likely source. The information may be applied to lipid extracts analysed from the laminated sediment formed in Loe Pool.

3.9.2 Features of a Lipid Extract

Many organisms synthesise a series of compounds by the process of carbon-chain elongation with acetate units (Cranwell, 1982). Biosynthesis of carbon molecules often produces a series differing by two carbon numbers which is termed a homologous series. In a review of lipids in aquatic sediments, Cranwell (1982), describes how homologous series can be characterised by their carbon number

range, their carbon preference index and the modality of their carbon number distribution. For example, extracts of n-alkanes from terrestrial plants show a dominance of odd over even carbon number molecules.

The carbon number range present in sediment can be characteristic of precursor organisms. Some classes of plants synthesise carbon molecules over different number ranges. However, changes in all or part of the range may occur during the processes of transport, sedimentation and diagenesis. The stability of each molecule is a factor of environmental conditions, molecule size and class. Degradation preferentially occurs with low carbon number molecules over higher chain length structures. Cranwell (1981.) reports that stability of free lipids decreases in the order of n-alkanes, alkan-2-ones, sterols, n-alkanoic acids, n-alkanols, n-alkenoic acids.

The carbon preference index (C.P.I.) is the ratio of odd to even carbon molecules. For normal hydrocarbons the C.P.I. is usually expressed by:

$$\text{CPI} = \frac{\Sigma \; 2 \; \text{X odd C 21-to-C 31}}{\Sigma \text{even C 20-to-C 30} + \Sigma \text{even C 22-to-C 32}}$$

(Cooper & Bray, 1963).

The C.P.I. of a particular range of molecules can be indicative of source. For example, in an n-alkane distribution, a high C.P.I. is characteristic of a higher plant origin. In contrast a low C.P.I. may be characteristic of a bacterial origin. Bacteria do not show a prominent carbon preference in their lipid composition (Cranwell, 1982)

Within a homologous series, carbon numbers may peak around certain

carbon numbers. A range with one peak is termed unimodal with a distribution around that point. If there are two associations then the series is called bimodal, with possibly one of the modes being dominant over the other.

3.9.3 Lipids of Aquatic Sediments

3.9.3.1 Normal Alkanes

Normal alkanes (n-alkanes) are straight chain hydrocarbons with the general formula $C_n H_{2n} +2$. An example is the C17 hydrocarbon n-heptadecane (Fig. 25). Alkanes have been widely reported in lacustrine sediments (Barnes & Barnes, 1978; Cranwell, 1982). They are found in the sediments of both oligotrophic and eutrophic lakes (Meyers & Takeuchi, 1979; Cardoso et al., 1983).

Alkanes in an oligotrophic lake are principally derived from an allochthonous source because lake productivity and hence aquatic input is low. Cranwell (1982) reports that typical carbon number ranges are from C 17-C 35 with a unimodal distribution within the range C 27-C 31. The distribution would have an odd over even-predominance and a C.P.I. greater than 4.0. An example is Loch Clair sediment with a carbon number range C 17 to C 35 (Fig. 26). The n-alkanes are in a unimodal distribution peaking at C 31, and a C.P.I. from 2 sections analysed of 5.5 and 7.7 (Cranwell, 1981). Such a distribution is indicative of a higher plant input (Eglinton & Hamilton, 1967; Simoneit, 1977; Barnes & Barnes, 1978; Cranwell, 1981 ; Cranwell,1982) Higher plants are known to have a similar

n-heptadecane

7-methyl heptadecane

8-methyl heptadecane

pristane

phytane

2,6,10-trimethyl-7(3-methyl pentane) dodecane

perylene
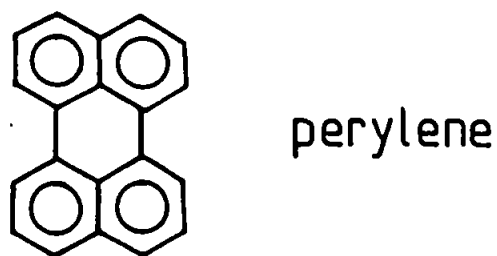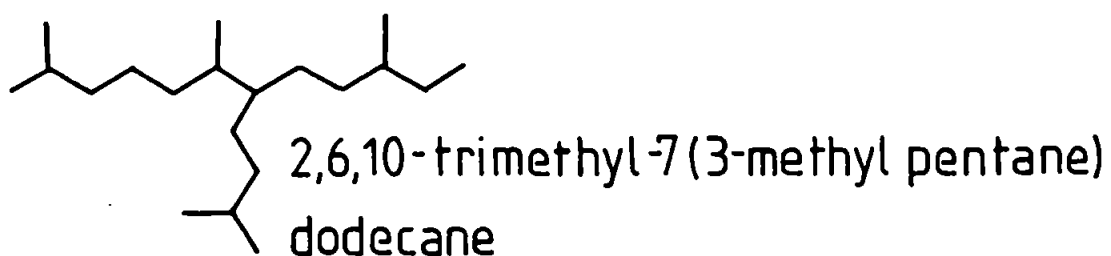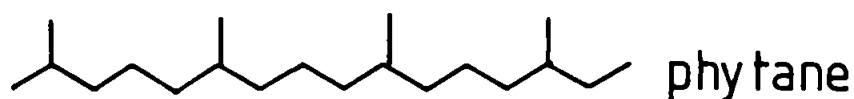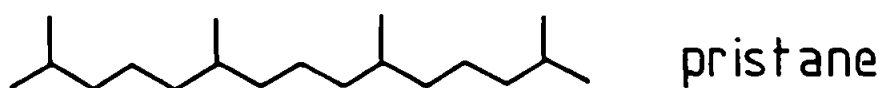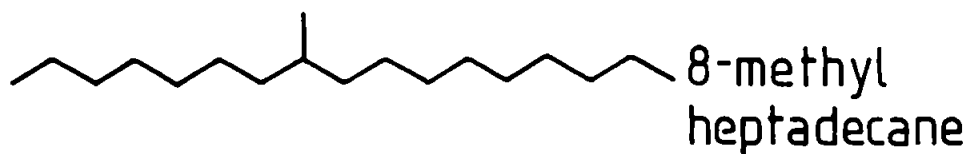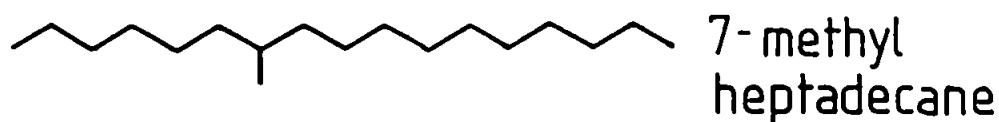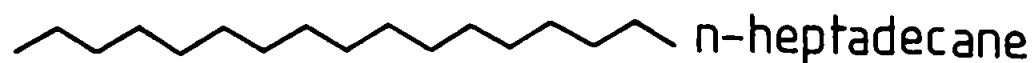
Figure 25. Structures of selected lipids (cont.).

OH   dodecanol

O
dodecanoic
OH   acid

benzo(e)pyrene

C 12 alkyl ester
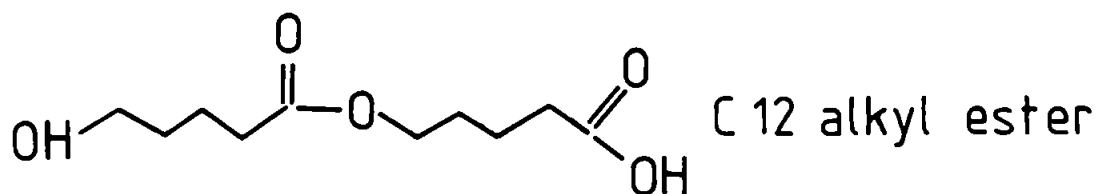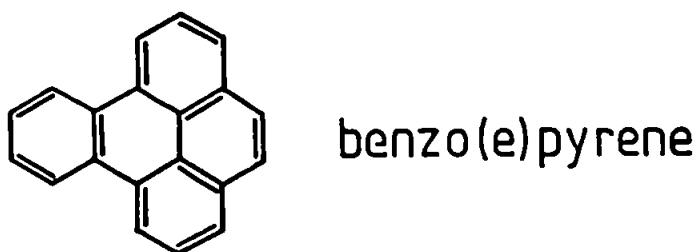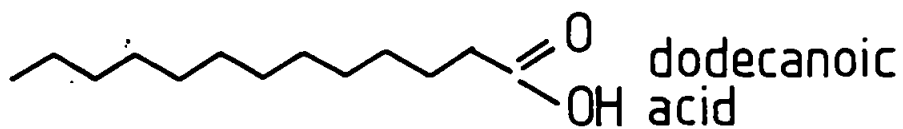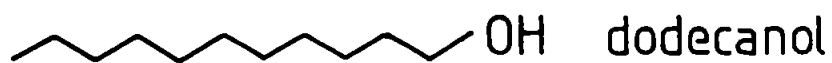
Figure 25 (cont.) Structures of selected lipids.
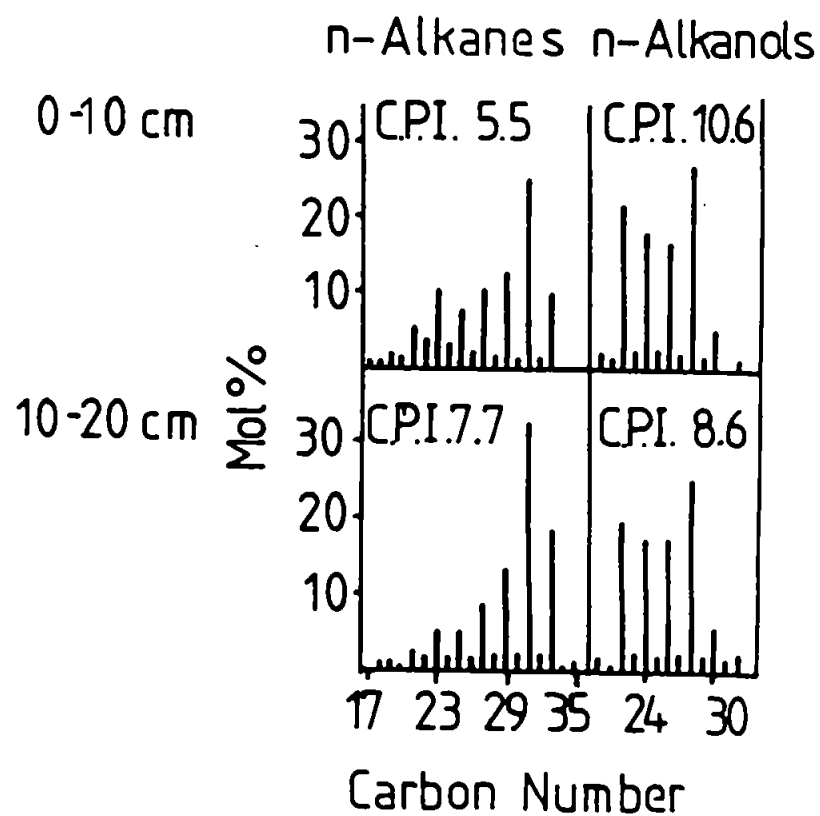
Figure 26. Percentage composition of free n-alkanes and
n-alkanols in Loch Clair, C.P.I. for n-alkanes
show odd-even ratio, those for n-alkanols show
even-odd ratio (from Cranwell, 1981b).

distribution of alkanes in their surface waxes (Kolattukudy & Walton, 1972; Kolattukudy, 1975; Tulloch, 1976).

The n-alkane distribution in eutrophic lakes is typified by a carbon number range of C 15 to C 35 with a bimodal distribution peaking round C 17 and C 29 to C 31,and a C.P.I. of 2-4 (Cranwell, 1982). An example of this distribution is found in the uppermost sediments of Rostherne Mere, (Cardoso et al., 1983). This is a highly productive lake with permanent stratification in the deepest part (Reynolds, 1979). Extractable lipids from the surface sediment have a carbon number range of C 17 to C 34 in a bimodal distribution peaking at n-C 17 and with a secondary point at n-C 29 (Fig. 27). The n-alkanes have a C.P.I. of 3.90. The mode around n-C 17 has been attributed to input from algae produced within the lake. Studies have shown that n-heptadecane is found widely in algae (Han et al., 1968; Gelpi et al., 1970; Bird & Lynch, 1974; Cardoso et al., 1983).

Normal alkanes are considered quite stable components of the lipid fraction (Cranwell, 1981b). They are subject to decay in anaerobic conditions (Giger et al., 1980). Short-chain alkanes may be microbially degraded more rapidly, so the presence of n-C 17 in sediment may only provide a qualitative rather than a quantitative record of algal populations (Cranwell, 1982).

An in situ distribution of n-alkanes may be produced by microbial activity. Evidence of a bacterial input is a low C.P.I. Microbes do not show a distribution with even or odd carbon numbers predominating (Cranwell, 1976). Such a C.P.I. may suggest rapid diagenesis of the more labile autochthonous input.
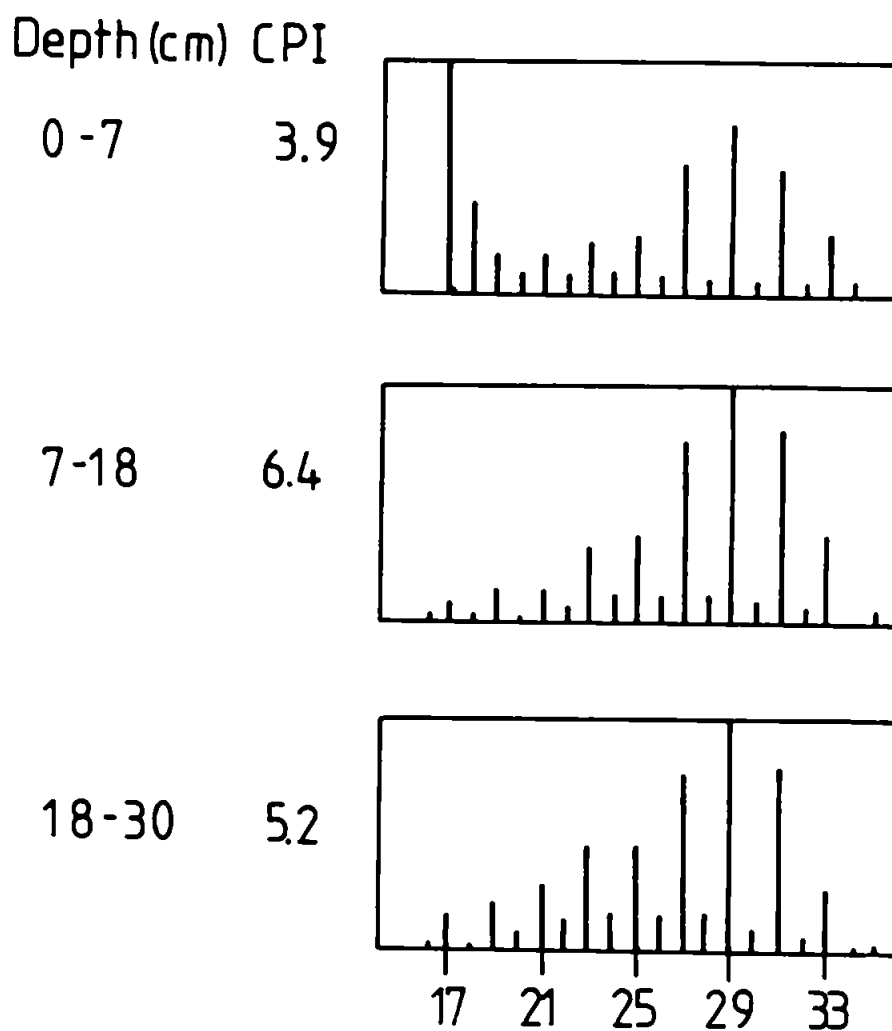
Figure 27. Carbon number distributions of straight-chain alkanes
from Rostherne sediment
(from Cardoso et al., 1983).

3.9.3.2 Branched-Chain and Cyclic Saturated and Unsaturated Hydrocarbons

Branched-chain and cyclic hydrocarbons occur widely in lacustrine sediment and have been used as markers of both the allochthonous and autochthonous input and to assess the palaeo-redox conditions of sedimentation.

Extracts from some lacustrine sediments contain a "hump" of unresolved and presumed branched-chain and cyclic alkanes. Such a chromatographic feature is termed an unresolved complex mixture (U.C.M.). In Greifensee, Switzerland, a U.C.M. was present in the lipid extract. The source was identified as a natural input from erosion of sedimentary rocks, that is, an allochthonous input (Giger et al., 1980). Other workers have found evidence of a pollution source from oil spills. For example, Quirke et al. (1980) found crude oil derivatives in a branched/cyclic alkane extract from Rostherne Mere.

Some short-chain branched hydrocarbons have been isolated from algae and sediment. For example, 7-and 8-methyl heptadecanes (Fig. 25) have been found in Rostherne Mere sediment and the blue-green alga, Microcystis sp.(Han et al., 1968; Gelpi et al., 1970; Eglinton , Maxwell & Philp, 1974; Brookes et al., 1976; Philp, et al. 1978). The presence of 7-and 8-methyl heptadecanes and other short-chain branched hydrocarbons quoted in the literature (Barnes & Barnes, 1978) infer an autochthonous input from a productive lake.

Two major components of a typical lacustrine sediment extract are

pristane and phytane (Fig. 25). They may be derived from waste oil as a pollution input (Cardoso et al., 1983), from erosion of oil bearing rocks (Giger et al., 1980), from ferns (Lytle, Lytle & Caruso, 1976), diatoms (Tornabene, Kates & Volcani, 1974), algae and bacteria (Han et al., 1968) or as derivatives of phytol (Ikan, Baedecker& Kaplan, 1975).

Didyk et al. (1978) and references therein suggest that phytol may degrade via an oxidative pathway to form pristane and by a reductive mechanism to form phytane. The pristane:phytane ratio has been used to assess the redox conditions of oil formation in ancient environments (Brookes, Gould & Smith, 1969; Powell & McKirdy, 1973). Didyk et al.(1978) hypothesised that such a measure may be used in recent sediments to assess palaeo-environmental redox conditions. The significance of this for Loe Pool is that the pristane:phytane ratio may differentiate between sediment deposited under oxidising and reducing conditions. The technique may therefore be able to identify the palaeo-redox conditions of individual laminations in the sediment column. This would be based on the assumption that pristane or phytane are not present from any other source.

3.9.3.3 Aromatic Hydrocarbons

Sedimentary polycyclic aromatic hydrocarbons (P.A.H.) are derived from anthropogenic activity (Hites et al., 1980; Heit et al., 1981), from early diagenetic reactions of terrestrially derived material (LaFlamme & Hites, 1978) and by biosynthesis in sediment (Louda & Baker, 1984). The so-called pollution input of

P.A.H. from anthropogenic activity is produced from the combustion or spillage of fossil fuels. Anthropogenic P.A.H., for example, benzo (e) pyrene (Fig. 25) occur widely in aquatic systems (Ishiwatari & Hanya, 1974; Neff, 1979). Their presence in the sediments of Lake Washington was interpreted as being the result of stormwater run-off carrying petroleum derived compounds (Wakeham, 1977). The presence of anthropogenic P.A.H. in lake sediment may infer an allochthonous source.

Perylene (Fig. 25) is the major P.A.H. in many aquatic sediments (Orr & Grady, 1967; Aizenshtat, 1973; Ishiwatari & Hanya, 1975; Simoneit, 1977; Simoneit, 1978; Brassell, 1980; Brassell et al. 1980a). The specific origin of perylene is unknown. Louda and Baker (1984), in a review of the literature, suggest that sedimentary perylene concentrations are highest where the overlying waters are productive and the hypolimnion is anoxic. The relative concentrations of perylene may potentially be used to distinguish between sediment formed in the summer under those conditions, from that deposited in the winter. Care should be taken with interpreting results of perylene because the concentration of this compound appears to increase with depth in the first few metres of sediment. This implies an in situ production of perylene from an unknown precursor.

3.9.3.4 Alkyl Esters

Alkyl esters are high molecular weight compounds of the general formula RCOOR', where R and R' (Fig. 25) are an alkanoic acid and an alkanol respectively. Alkyl esters have been reported in aquatic

sediment, both in eutrophic lakes (Cranwell, 1983; Fukushima & Ishiwatari, 1984/85), in oligotrophic lakes (Cranwell & Volkman, 1981; Fukushima & Ishiwatari, 1984/85) and in a diatomaceous ooze (Boon & DeLeeuw, 1979).

Alkyl esters isolated from the oligotrophic Loch Clair had a carbon number range C 38 to C 50 (Fig. 28) with a unimodal distribution peaking at C 44 (Cranwell & Volkman, 1981). This was considered to be characteristic of a higher plant source. Alkyl esters with a similiar carbon number distribution have been reported in leaf waxes of higher plants (Kolattukudy, 1976; Tulloch, 1976; Tulloch & Hoffman, 1979).

Analysis of eutrophic lake sediments from Upton Broad (Fig.29) and Crose Mere isolated mainly C 24 to C 36 saturated constituents, with some branched esters. In some extracts an additional mode of straight-chain saturated C 38 to C 50 esters of terrestrial origin was present (Cranwell, 1983). The author concluded that the lipids were formed by microbial action because of the similarity in molecular composition of corresponding branched-chain esters from the two sites.

Work by Fukushima and Ishiwatari (1984/85) is in broad agreement with results and conclusions reached by Cranwell and co-workers. They reported that in sediments of oligotrophic lakes the wax esters were mainly normal long-chain molecules. In contrast eutrophic lake sediments contained wax esters with shorter-chain length molecules with a greater proportion of branching.

Diatoms are a further aquatic source of alkyl esters. Analysis of a diatomaceous ooze revealed the presence of wax esters in the carbon number range C 32 to C 44 in a unimodal distribution peaking
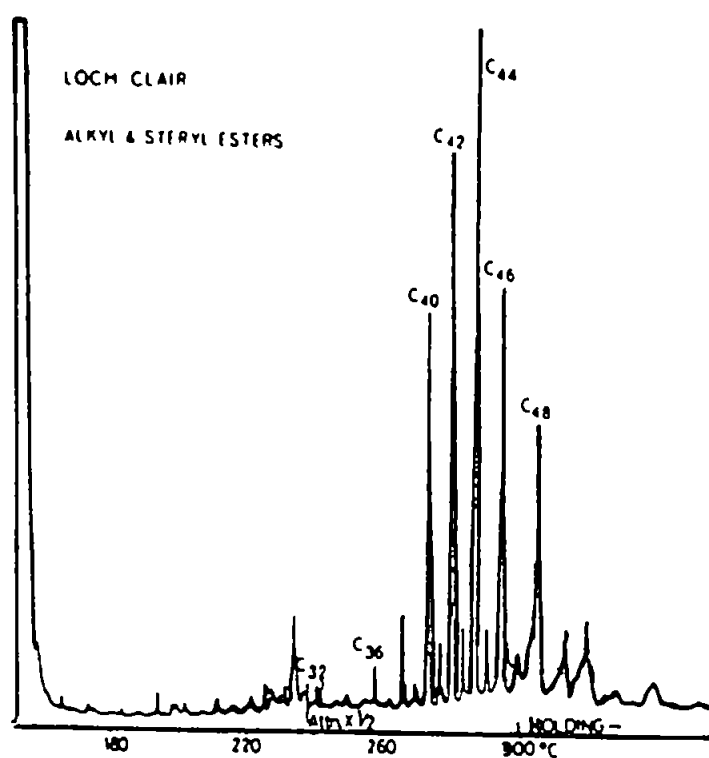
Figure 28. Gas chromatogram of fraction containing alkyl and steryl esters isolated from Loch Clair sediment (0-10cm). Conditions : 6m x 0.3mm OV-1 column, temperature programmed from 150°C to 305°C at 4°/min. He carrier gas at 1.5 kg cm^{-2} inlet pressure (from Cranwell and Volkman, 1981).
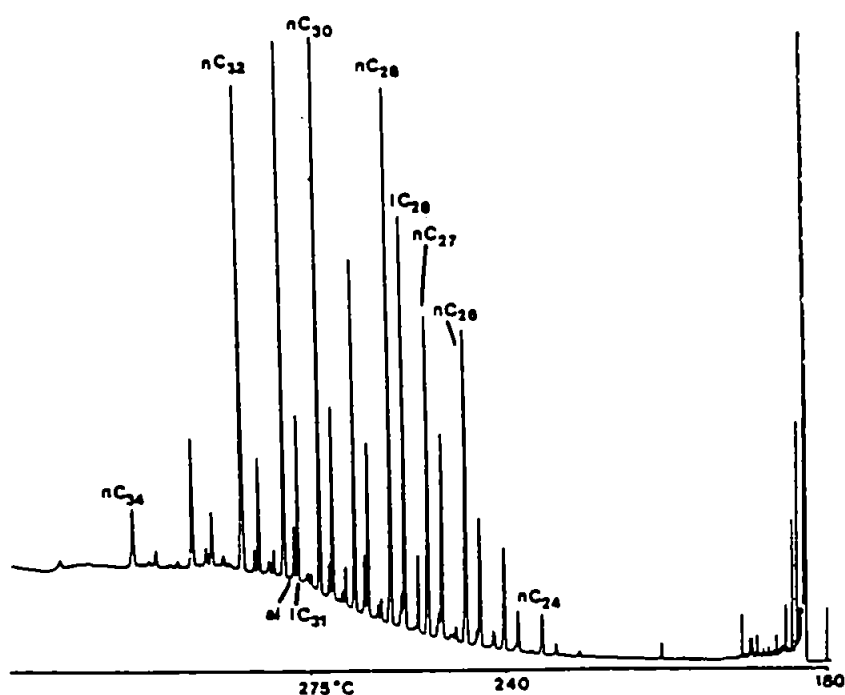
Figure 29. Gas chromatogram of saturated alkyl esters from Upton
Broad sediment (0-6cm). Conditions : vitreous silica
capillary column (25m x 0.25mm i.d.) coated with
SE-30, temperature programmed 180-275°/3°/min.,
using hydrogen as carrier gas at 0.5 kPa inlet
pressure and flame ionisation detector
(from Cranwell, 1983).

around C 38 to C 40 (Boon & De Leeuw, 1979).

Distributions of wax esters may, therefore, be used to infer an allochthonous input, microbial activity and the presence of zooplankton.

3.9.3.5 Normal Alkanols

Homologous series of n-alkanols have been reported in lipid extracts of lacustrine sediments (Cranwell, 1977b; Cranwell, 1978; Cranwell, 1981b; Shigaraki & Ishiwatari, 1981). n-Alkanols from the oligotrophic Cam Loch occur with a high even over odd C.P.I. (Cranwell, 1977b). The series peaks at either C 26 or C 28 with at certain depths a secondary peak at C 22. The n-alkanols C 16 to C 21 form only a small percentage of the extract.

A similar distribution was found in the oligotrophic Loch Clair. Cranwell (1981b) reported a range from C 20 to C 32 maximising at C 28 with a secondary peak at C 22 and C.P.I. range of 10.6 to 8.6 even over odd predominating (Fig. 26). Extractable n-alkanols from the eutrophic Crose Mere also had a high C.P.I., with a value of 9.60 (even over odd predominance). This extract had a bimodal distribution peaking at C 26 (Fig. 30) with a secondary mode around n-C 16 (Cranwell, 1978).

The range C 22 to C 32 has been attributed to a higher plant or allochthonous input. Higher plants are reported to contain alkanols in the C 22 to C 26 range (Tulloch, 1976). Lower-chain length alkanols, which are found in lower plants, are considered to be labile in lake waters and sediment (Cranwell, 1981), so no
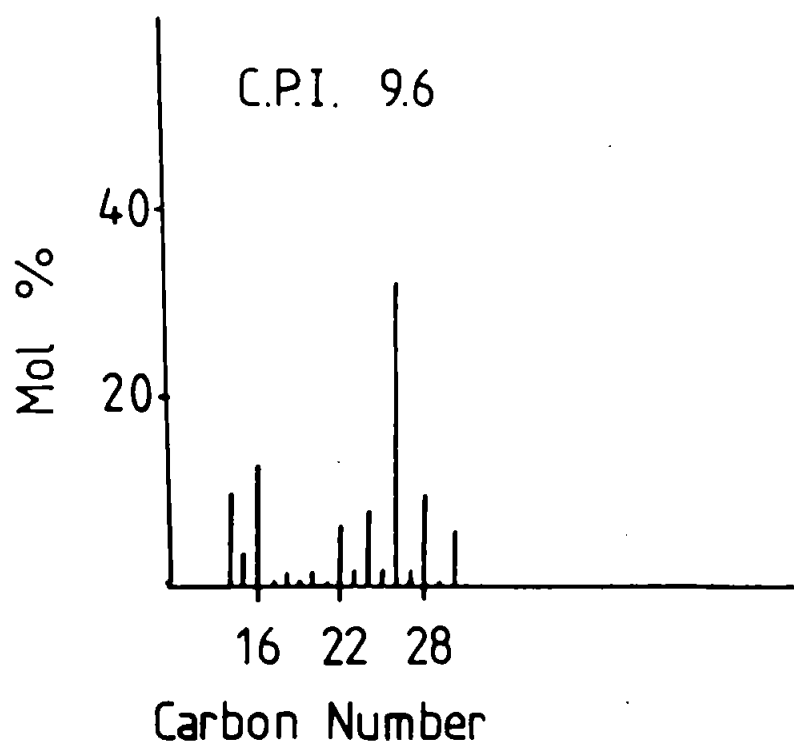
Figure 30. Percentage composition of free n-alkanols in
Crose Mere sediment
(from Cranwell, 1978).

input is commonly found from lower plants. In the eutrophic Crose
Mere the secondary mode around C 16 was attributed to the microbial
hydrolysis of esters in which C 14 and C 16 were major n-alkanols
(Cranwell, 1981b). Wax esters with the short-chain length alkanols
are not from terrestrial sources but are themselves indicative of
either autochthonous aquatic input or of bacterial action (section
3.9.3.4)

Straight-chain alkanols may be used to identify the allochthonous
component and possibly a microbial or lower plant input.

3.9.3.6 Normal-Alkanoic Acids

Normal alkanoic acids (Fig. 25) occur ubiquitously in lacustrine
sediment (Eglinton & Hunneman, 1968; Cranwell, 1974; Brookes et
al., 1976; Cranwell, 1977b; Matsuda & Koyama, 1977; Cranwell,
1978; Ishiwatari et al., 1980; Meyers, Maring & Bourbonniere,
1980; Shigaraki and Ishiwatari 1981; Cardoso et al., 1983). A
typical eutrophic lake distribution of n-alkanoic acids is found in
Rostherne Mere (Cardoso et al., 1983). The carbon number range
is from C 12 to C 34 with an even over odd predominance (Fig. 31).
The distribution is bimodal with peaks around C 16 and C 24 to C
26.

Alkanoic acids may degrade in sediment, generally shorter-chain
compounds being more labile than the long-chain components. Cardoso
et al. (1983) demonstrated this by the analysis of alkanoic
acids at depths of 0-7 cm, 7-18 cm and 18-30 cm from Rostherne
Mere sediment. The major mode changes from around C 16 to C 24 to C

26 down the core and the C.P.I. also decreases with depth in the sequence 13.90 to 6.80 to 6.0 (Fig. 31).

In general terms n-alkanoic acids with chain lengths less than 20 have a presumed lower plant and predominantly autochthonous input. In contrast, those distributions with carbon chain lengths greater than 20 have a likely allochthonous higher plant origin (Eglinton et al., 1962).

However, care must be taken with interpretation of these distributions because degradation of terrestrially-derived alkanoic acids can reduce the input and degradation of terrestrially-derived alkyl esters can liberate the acid moiety.

Aquatic sediment contains a complex mixture of many thousands of lipids. Some of these may be characteristic of their origin and the processes occurring during their transfer from source to the lake sediment environment. This review indicates that selected classes of lipids extracted, separated and analysed from aquatic sediment have the potential for providing evidence of sediment source, season of deposition and certain limnological conditions.
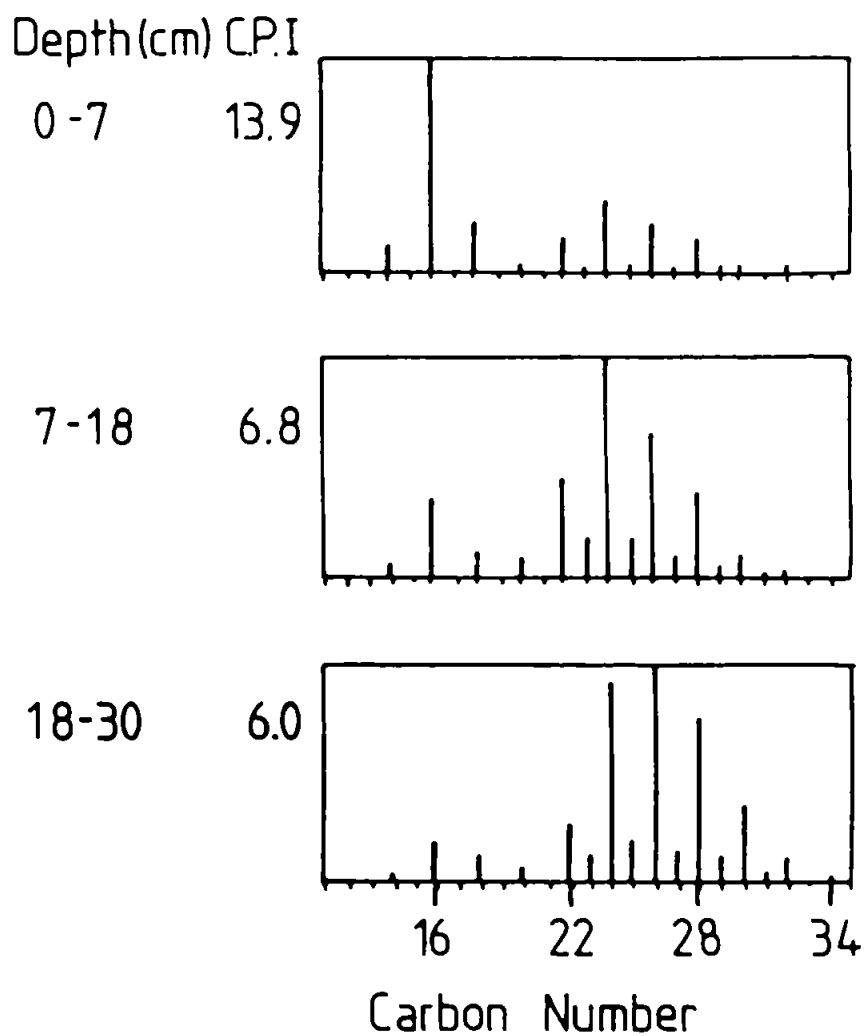
Figure 31. Carbon number distributions of straight-chain alkanoic acids from Rostherne Sediment (from Cardoso et al., 1983).

Chapter 4 Experimental

4.1 Core Collection

Sediment was obtained using two basic types of coring equipment, the Mackereth 1m Mini-corer (Mackereth, 1969) and the freezer sampler (Swain, 1973; Huttunen & Meriläinen, 1978).

The Mackereth Mini-corer collects approximately 1m of "wet" sediment in a perspex tube. The apparatus is particularly suitable for the rapid collection of lake sediment cores. Some smearing of material occurs during both coring and extrusion of the sediment, especially the upper 10cm of sediment which has a very high water content.

Most of the work presented in this study is based on sediment cored by a freezing sampling technique. This method collects solid cores which have the advantage that whole undisturbed sections can be removed without the destruction of fine laminations.

Two types of freezer sampler were used, the "icy finger" sampler (Swain, 1973) and the "box freezer" corer (Huttunen & Meriläinen, 1978). The icy finger is a hollow cylindrical metal tube fitted with a pointed nose cone (Fig. 32). The bottom of the sampler is weighted with lead. At the top there is a detachable lid with a gas release hole and sockets for the attachment of ropes. The version used in this work was designed by Coard (in prep.) and had a length of 1.5m.

The box freezer corer was designed by Huttunen and Meriläinen
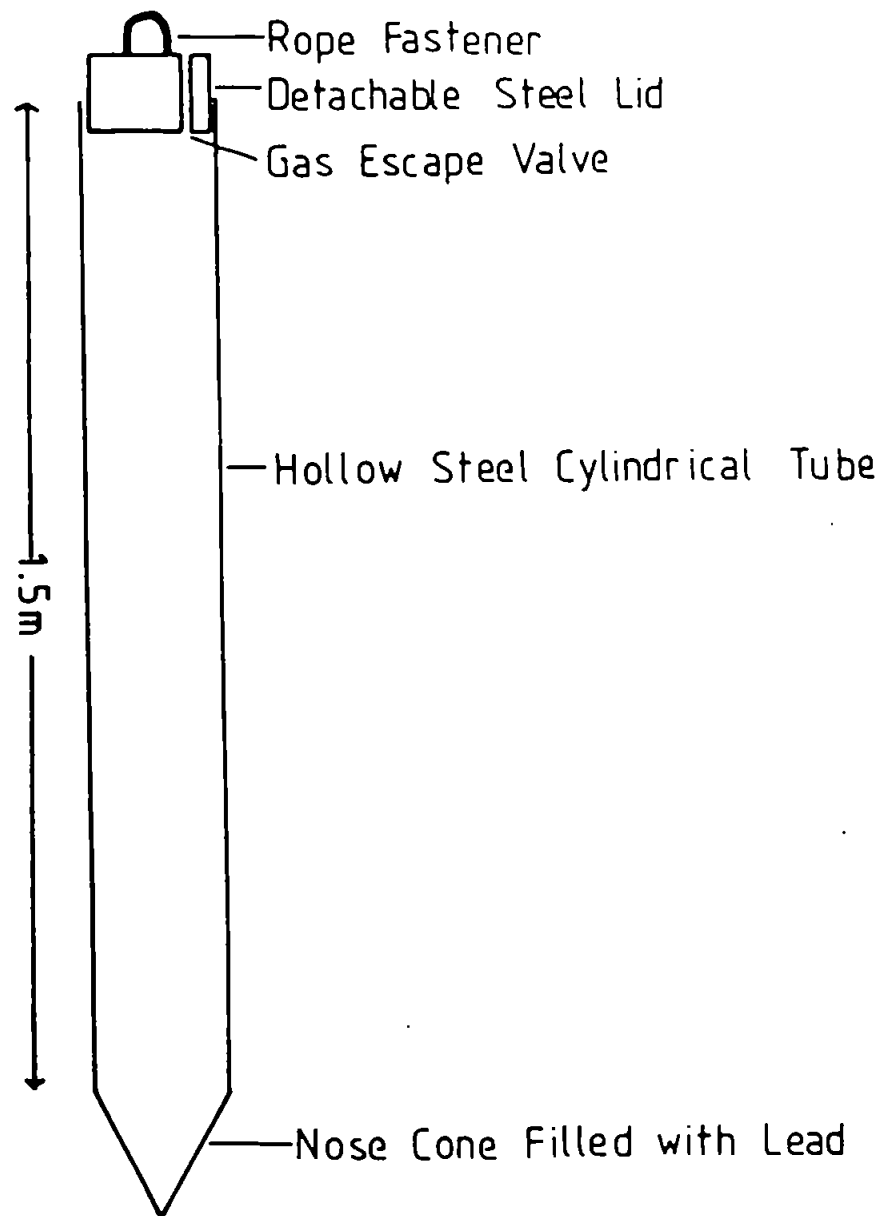
Figure 32. Diagram of Icy Finger used at Loe Pool
(modified from Swain, 1973).

(1978). A version was built at the Polytechnic, with minor modifications by Coard (in prep.). The corer is a steel box 30cm x 100cm x 5cm, and has a pointed keel and detachable lid with gas escape valve (Fig. 33).

Each of the freezer samplers was operated in a similar manner. The corer was filled with solid carbon dioxide in a granular or pelleted form. To collect a sediment core the filled sampler was taken to the coring location in an inflatable boat. Prior to coring a low freezing point solvent such as acetone was added. This acted as a heat dispersant and accelerated the freezing process. The lid was placed on the corer and it was held over the side of the boat. When released it fell swiftly through the water column and became embedded in the sediment. The corer was left for about 10-12 minutes before retrieval. This allowed approximately 2-5 cm of material to accumulate. The "icy finger" produced a hollow cylindrical core and the "box freezer" a flat sediment section. Once collected, cores were removed from the freezer samplers by gentle thawing.

It was found by experience that the "box type" freezer sampler produced less disturbed cores and gave a larger amount of sediment for each lamination. It was also more suitable for multiple coring because the sample could be removed with relative ease. In contrast, the icy finger had the advantage that it penetrated to a greater depth.

4.2 Core Transport and Storage

Mackereth cores were transported and stored upright in a rack. In

- 117 -
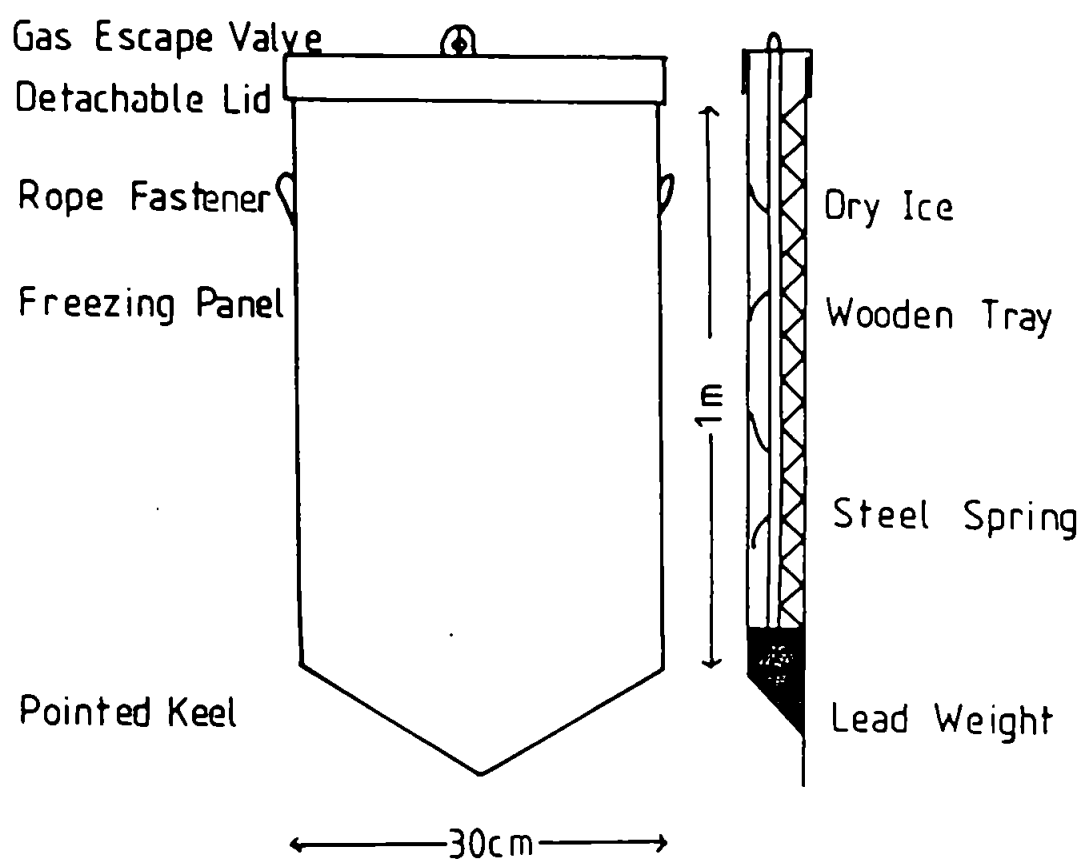
Figure 33. Diagram of Box Freezer Corer used at Loe Pool
(from Huttunen and Meriläinen, 1978).

the laboratory the cores were stored in a dark 4 $^{\circ}$C room. Samples from the freezer corer were wrapped in aluminium foil to prevent photoxidation and transported frozen. Storage was in a freezer at approximately -10 $^{\circ}$C.

4.3 Core Processing

4.3.1 Mackereth Cores

Extrusion and sectioning of Mackereth cores was performed in the laboratory. The core was clamped upright and the bottom bung replaced by a tight fitting bung small enough to travel up the inside of the perspex tube. The top bung was removed. A 1 cm perspex collar was placed over the top of the tube. To extrude the core the bottom bung was pushed upwards until the sediment reached the top of the collar. In order to remove a 1cm slice, a very thin perspex sheet was inserted between the top of the core tube and the collar. Slices were stored in plastic petri dishes prior to use.

4.3.2 Freezer Corer Samples

On removal of the cores from the lake, partial slumping of wet sediment occurred down the front of the core. This smearing was removed in the laboratory by first washing the surface of the sediment with water. Final cleaning was achieved by scraping away extraneous material. This was carried out along the direction of the lamination to prevent contamination of one lamination with another. Once cleaned, each core was photographed to provide a

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record of. the stratigraphy.

To cut out sediment from the frozen core, the sample was allowed to thaw gently. Once sufficiently soft, but still retaining its structure, the sediment was sliced. A scalpel was used for thin slices and an electric carving knife with blades fitted for frozen food for larger sections. The electric carving knife had the advantage of greater speed, but the disadvantage of the loss of approximately 0.5 cm of sediment with each cut. All core cleaning and extraction procedures were carried out in subdued light in order to minimise possible photodegradation of labile compounds.

4.4 Techniques

4.4.1 Photography

·Photography was performed by Mr Steve Johnson from Media Services, Plymouth Polytechnic. Pictures were taken with a Cambo 5"x4" Technical Camera synchronised with electronic flash illumination. The infrared photographs were taken using a Kodak Wratten 88A filter and Kodak High Speed Infrared black and white 5"x4" film, developed in D.76 solution. Colour plates were taken from Kodak Vericolor II Professional Type S 5"x4" colour negatives.

4.4.2 Analysis of Dry Weight, Loss on Ignition and Combustion
Residue

The method used was adapted from Bengtsson (1979). A porcelain crucible (5ml) was ignited (550 $^{\circ}$C, 1hr.) in a muffle furnace,

allowed to cool in a desiccator and weighed to an accuracy $\pm$ 0.1 mg. A small aliquot of sediment (0.5-1.0g) was placed in the crucible, weighed and dried in an oven (105°C, 24 hr.). Once dried it was cooled in a desiccator and reweighed. The crucible was then placed in a muffle furnace and ignited (550 °C, 2hr.). The sample was transferred to a desiccator, allowed to cool and reweighed. From the figures obtained, dry weight (D.W.) per gramme wet weight, loss on ignition (L.O.I.) per gramme dry weight and combustion residue (C.R.) per gramme dry weight were calculated using the following equations:

$$D.W. = \frac{\text{weight dry sediment}}{\text{weight wet sediment}} \quad \text{g/g wet sediment}$$

$$L.O.I. = \frac{\text{weight dry sediment-weight ignited sediment}}{\text{weight dry sediment}} \quad \text{g/g D.W.}$$

$$C.R. = \frac{\text{weight ignited sediment}}{\text{weight dry sediment}} \quad \text{g/g D.W.}$$

Duplicates were run for each sample and an average was calculated.

4.4.3 Magnetic Measurements

4.4.3.1 Preparation of Samples

Samples were dried either in an oven (40 °C, 24hr.), or in a freeze drier. The sediment was lightly ground and packed into pre-weighed plastic containers (10cc.) and reweighed. Sample weights were in the range 3-8g, depending upon quantity of sediment

available. Foam rubber was packed tightly on top of the dry sediment to prevent movement of grains and the container was then capped.

4.4.3.2 Measurement of Magnetic Susceptibility

Magnetic susceptibility was measured with a Bartington Instruments Magnetic Susceptibility Meter MS1, using a type MS1B sensor.

4.4.3.3 Measurement of Saturated Isothermal Remanent Magnetism and S Ratio

Samples were placed in a Molspin pulse magnetizer and saturated with a field of 8,000 Oersteds (Oe), (0.8T). The Saturation Isothermal Remanent Magnetism was measured in a Molespin Fluxgate Spinner Magnetometer. The samples were then placed in a second Molespin Pulse Magnetizer and a backfield of 1,000 Oe, (0.1T) was applied. The remanent magnetism was remeasured using the Magnetometer.

4.4.4 Determination of the Concentration of Metals

4.4.4.1 Extraction

A hot extractable technique adapted from Maynard & Fletcher, (1973) was used. Freeze-dried sediment (0.2-1.0g) was transferred to a preweighed Pyrex beaker (50 ml). Dilute hydrochloric acid was added (0.5N HCl, 10ml) and the sample was boiled for 20

minutes. The extract was cooled and filtered (Whatman No. 1 Qualitative) into a volumetric flask (25 ml). The solutions were made up with distilled water and then transferred to plastic storage bottles (50 ml). All glassware was acid-washed prior to use (1M HCl, 20mins) and a procedural blank was run.

4.4.4.2 Analysis

Analysis of iron, manganese, copper and calcium was performed on an I.L. 151 Atomic Absorption Flame Spectrophotometer in absorbance mode. Lead, cobalt, nickel and zinc were analysed on the same instrument with background correction. The calcium sample was treated with lanthanium chloride (1% solution) to prevent chemical interference from phosphate. Sodium and potassium were analysed using a Varian AA-975 series spectrophotometer in emission mode. Standard instrumentation conditions were set according to the manufacturers handbooks. Precision was assessed by repeat extraction and analysis. Coefficient of variation (C. of V.) values are quoted for each element analysed.

4.4.5 Analysis of Carbonate, Total Carbon, Organic Carbon and Nitrogen

Freeze dried sediment was ground with a mortar and pestle. Each sample was divided into two homogenous fractions and aliquots placed in glass vials (2ml). One of these fractions was placed in a vacuum desiccator with a beaker of concentrated hydrochloric acid

(100ml). The desiccator was evacuated, and the samples left until all inorganic carbonate had been destroyed (48 hr.). The following reaction occurred:

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$
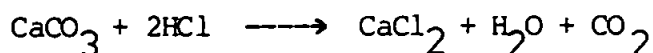
Following acid fuming, the sediment was redried and stored in an evacuated desiccator with the drying agent phosphorus pentoxide (2-4 days). Analyses were performed on a Carlo Erba Elemental Analyser mod. 1106 at the Institute of Marine Environmental Research. Samples were weighed using a Cahn 25 Automatic Electrobalance into small tin containers and then crimped. The following description of the analysis is described from a Carlo Erba Instrumentation Handbook:

Tin boats containing the sediment samples were dropped at preset intervals into a heated (1,050 $^{\circ}$C) vertical quartz tube. Flash combustion occurred in a helium atmosphere temporarily enriched with oxygen. Quantitative combustion was then achieved by passing the gases over Cr_2O_3. To eliminate excess oxygen the effluent flowed through copper at 650°C. These gases then passed into the heated chromatographic column (80°C) packed with Porapak QS. The individual compounds were separated and eluted in the order N_2-CO_2 -H_2O through a hot wire detector.

The range of the instrument was calibrated with the standard cyclohexanone-2,4-dinitrophenylhydrazone (C=51.79%, H=5.07%, N= 20.14%). Calibration was checked at the start and finish of an experimental run and standards were included at regular intervals. Several empty tin boats were also inserted to assess the blank value. As the response of the instrument was not linear over the entire working range, standards were only used over the same range

of carbon and nitrogen as occurred in the sediment samples. The precision was assessed by the coefficient of variation.

Total carbon, organic carbon and nitrogen values were obtained. Carbonate was calculated by difference between the total carbon and organic carbon figures.

4.4.6 Quantification of Humic Acids

The technique for analysis of Humic Acids was adapted from the method of Stevenson (1965). All glassware was acid-washed prior to use (HCl, 1M). Sediment with extractable lipids removed, was transferred to a preweighed centrifuge tube (100ml), freeze dried and reweighed. The sample was decarbonated by addition of hydrochloric acid (0.5N, 20ml), stirred, shaken (flask shaker, 2hr), centrifuged (4,500 rpm, 20 mins) and the resultant liquid pipetted off. Chloride residues were removed by shaking with water, centrifuging and decanting the aqueous waste. The sediment was freeze dried and reweighed. Sodium hydroxide (0.5N, 50ml) was added and shaken (flask shaker, 6hr). Residue deposited on the sides of centrifuge tube was washed down with distilled water. The sediment was centrifuged (4500 rpm, 20 mins) and the liquid pipetted into a round bottomed flask (250ml). The sediment was treated twice more with sodium hydroxide and the extracts combined. Concentrated acid (HCl, approx 20ml) was added until humic acids were precipitated, leaving fulvic acids in solution. The fulvic acids were removed by centrifuging and washing processes. The humic acid residue was rewashed (x2 distilled water, 20ml) to remove chloride, filtered on-to preweighed Whatman GF/F filter paper, freeze dried and

reweighed. Results were expressed as humic acid per gramme dry weight sediment.

4.4.7 Analysis of Sedimentary Pigments

4.4.7.1 Spectrophotometric Technique

The method used was adapted from Strickland and Parsons (1972). A known weight of sediment (c. 1g) was placed in a graduated centrifuge tube. Acetone:distilled water (9:1) was added to a constant volume (10 ml). The sediment was stirred and the tube capped and placed in a sonic bath to aid extraction (10 mins). Extraction continued in a refrigerator (3 hrs). The sediment was separated from the acetone:distilled water solution by centrifuge (4,000 rpm, 10mins). The pigment extract was decanted into a cuvette (optically matched glass, 1cm path length). This was tested for absorption (Perkin-Elmer 522 Spectrophotometer scanning 750-350 nm) and values were noted at 665, 645 and 630 nm.

The weights of the sedimentary pigment degradation units were expressed per unit chlorophyll a according to the formula given by Stricklands and Parsons (1972):

$$pigment = \frac{c}{v} \times 10 \quad mg/g \ dry \ weight$$

where c (chlorophyll a) =11.6 E665 - 1.31 E645 - 0.14 E630

v = weight dry sediment in grammes

and E = absorbance.

4.4.7.2 High Pressure Liquid Chromatography-Coupled

Absorbance and Fluorescence Detection

Pigments were extracted by placing frozen sediment (c. 1-3g) in a preweighed tissue homogenising tube. Acetone solution (acetone:distilled water 9:1, 2.5ml) was added and the sediment homogenised (2 mins). The solution obtained was decanted into a tube and centrifuged to remove particulates (4,000 rpm, 20 mins). The extract was decanted into a vial (2ml). Prior to injection, the sample was made up with an ion pairing agent (tetrabutylammonium acetate, 30%). Standard High Pressure Liquid Chromatography (H.P.L.C.) conditions were as follows:

Column: Hypersil C 18 O.D.S. reverse phase, length 25 cm, packing
   5μm, internal diameter 5mm.

Absorbance detector: Hewlett Packard 1,040a photodiode array
   detector, operating at   440nm.

This was controlled with a Hewlett Packard 85 micro computer and disc drive system. Absorbance scans were recorded on disc and could be reproduced on an interfaced XY plotter.

Fluorescence detector: Du Pont 836

   excitation $= 440 \pm 40$ nm

   emission $= \sim 600$nm

Quantification of pigments was achieved using the procedure outlined by Mantoura and Llewellyn (1983). The weight of carotenoid was estimated from an extension of Beer's law based on:

$$W \ (g) = \frac{(a \times At \times f)}{(Sw \times E\%440nm \times 100)}$$

Where   W (g) = the weight in grammes of pigment

a = peak area (cm squared)

At is the absorbance setting on the detector

f is the flow rate (cm cubed/min)

S is the chart speed (cm/min)

w is the full scale width of the chart (cm)

E%440nm is the specific extinction coefficient of the
pigment at 440 nm.

The value of E used was based on the extinction coefficient of
lutein which is 2393.

The chlorophylls a and b were quantified from their
fluorescence chromatograms after calibration with standards. The
amount of the other chloropigments was obtained by quantifying as
for chlorophyll a and then multiplying the value obtained, by
their relative fluorescence response with respect to chlorophyll
a. Values used were:

Chlorophyllide a	1.65	Phaeophorbide b	1.468
Phaeophorbide a	0.471	Phaeophytin b	0.697
Phaeophytin a	0.386	Chlorophyll c1 + c2	1.54
Chlorophyll b	0.22	Chlorophyllide b	0.129

(Llewellyn, pers. comm.).

4.4.8 Analysis of Sedimentary Lipids

4.4.8.1 Extraction and Separation of Sedimentary Lipids

The method used was adapted from Cranwell (1978) and an outline of
the experimental scheme is shown (Fig. 34). All glassware was
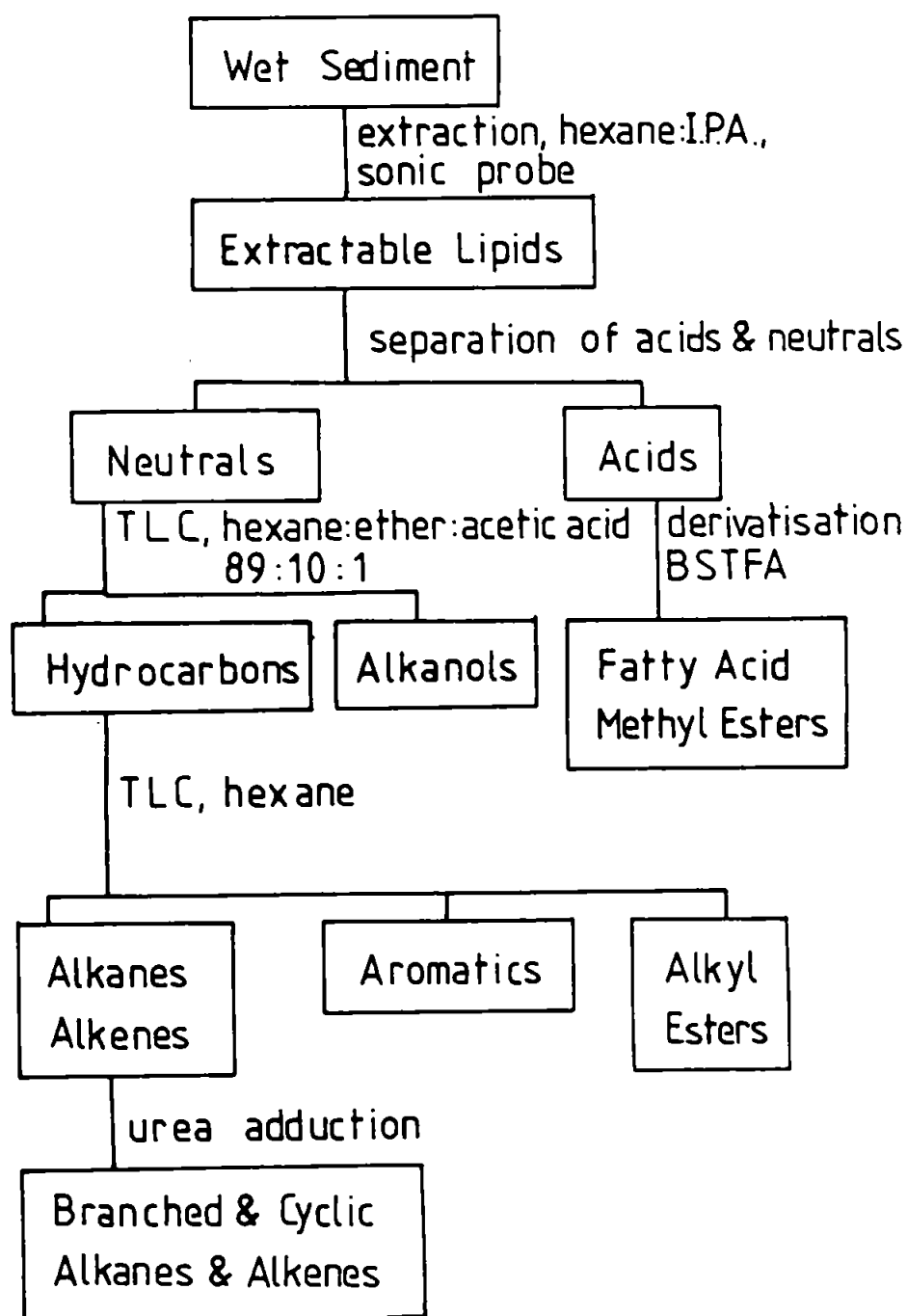
Figure 34. Outline of extraction scheme
(modified from Cranwell, 1978).

cleaned by soaking in chromic acid (12 hr.), rinsing with distilled water (x5) and then dried in a clean oven (105 $^{\circ}$C). All solvent was redistilled and in some cases doubly redistilled to remove contamination. Kieselgel 60G was cleaned by Soxhlet Apparatus (dichloromethane, 24 hr.). TLC plates were pre-eluted with ethyl acetate and a line drawn across the top to isolate any contamination. Cotton wool used in columns was defatted (dichloromethane soxhlet, 24hr). Water, potassium hydroxide (KOH), hydrochloric acid (HCl) and Mercury (Hg) were extracted with dichloromethane (x3) prior to use. A procedural blank was run for every process.

Frozen sediment from individual laminations (c. 20-25g wet weight, 60% water) was placed in a preweighed glass centrifuge tube (100ml). The lipids were extracted 5 times using the isopropanol:hexane (1:4, 20ml) ternary system (Dole & Meinertz, 1960), by ultrasonication (Dawe Ultrasonic Probe, 10mins) in an ice bath. The sample was centrifuged (2,500 rpm, 10mins) and the lipids pipetted into a round bottomed flask (250ml). The extracts were combined and concentrated (Buchi Rotary Evaporator, 25°C, water pump vacuum). The acid and neutral fractions were separated according to the method used by McEvoy (1983). The extract was saponified (6% KOH in methanol, 5ml) under nitrogen (12 hr.), transferred to a separating flask with water (5ml), methanol (1ml) and dichloromethane (3x5ml). The neutral fraction was obtained by shaking with dichloromethane (3x5ml) and separating the dichloromethane extract into a second separating flask. This was washed with water twice. The water fraction (separating flask 2) was combined with the original aqueous fraction (separating flask

1). The dichloromethane extract was decanted into a round bottomed flask (100ml) to form the neutral fraction. The aqueous fraction (separating flask 1) was acidified to pH 1 with concentrated HCl (c. 1ml) and extracted with dichloromethane (3 x 5ml) to form the acid fraction.

The neutral fraction was further separated by thin layer chromatography (TLC) on silica gel (Kieselgel 60G, 0.5mm) using hexane:diethyl ether:acetic acid (89:10:1, 100ml) as the eluent. Standards were run (octadecane, perylene, C26 alkyl ester and cholesterol). The fractions were viewed under ultra violet (u.v.) light (365nm) and separated into two fractions. The hydrocarbon fraction was rechromatographed by TLC (Kieselgel 60G, 0.5mm) using hexane (100%, 100ml) as the eluent. The plate was viewed under u.v. light (365nm) and three fractions separated. Compounds were eluted from the Kieselgel with dichloromethane. The branched-chain and cyclic hydrocarbons were separated from the hydrocarbon fraction by urea adduction (Fig. 34).

The alcohol and fatty acid fractions were derivatised prior to gas chromatographic (G.C.) analyses to their T.M.Si. ethers with N, O-bis(trimethylsilyl)trifluoroacetamide (BSTFA 40μl, hexane 80μl, 15 mins, 60 ^{o}C). Where necessary sulphur was removed from the hydrocarbon fraction by passage through an activated copper column (Blumer, 1957) and from the more polar fraction by shaking with elemental mercury (McEvoy, 1983).

4.4.8.2 Gas Chromatography

Analysis of lipid fractions was by a Carlo Erba 4160 High

Resolution Gas Chromatograph. The on-column injection system was used with hydrogen as a carrier gas. Typical chromatographic conditions were:

Column	J+W DB5 25m i.d. approx 0.3mm
Carrier gas	H2
Column pressure	0.4-0.5 Kg/cm squared
Detector	Flame Ionisation Detector, 350 °C
Detector gas flows	H2 30ml/min, air 300ml/min.
Attenuation	4
Chart speed	5mm/min
Temperature programme	40-320 °C at 4°C/min, 320°C isothermal 5-30 mins.

4.4.8.3 Computerised-Gas Chromatography-Mass Spectrometry

Analysis of certain lipid fractions was performed using a Computerised-Gas Chromatography-Mass Spectrometry (C-GC-MS) system for identification purposes. The instrumentation used was a Carlo Erba 5300 Mega Series Gas Chromatogram coupled with a Kratos M.S.25 Mass Spectrometer. Data acquisition was by a D.S.55 system and processing using the D.S.90 system on a Data General computer. Typical C.-G.C.-M.S. conditions were:

Column	J+W DB1 25m
Injection mode	On column
Carrier gas	Helium
Temperature programme	40 °C 2.5 mins, 40-300°C at 4°C/min, 300 °C isothermal 5-20 mins

Ionisation voltage   50 eV

Scanning rate   0.5 decades per second

Ion source temperature   250 ^{o}C.

4.4.8.4 Identification of Extractable Lipids

The identity of compounds was established on a number of parameters. These were:

1)   T.L.C. rF value

2)   T.L.C. co-elution with authentic standard

3)   G.C. chart retention time

4)   Co-elution with authentic standard on G.C.

5)   Extrapolation of homologous series on G.C.

6)   C.-G.C.-M.S. mass spectrum analysis

7)   C.-G.C.-M.S. mass fragmentogram analysis

         (particularly to identify homologous series).

Not all identification parameters were used for each lipid fraction. C.-G.C.-M.S. analysis was particularly limited by a very substantial "downtime" period.

4.4.8.5 Quantification of Lipid Fractions

Quantification was established on peak area . The Carlo Erba 4160 H.R.G.C. was coupled to an Apple 2E microcomputer with Chromatochart software.

The first chromatogram of each day was a standard mixture of:

Compound	Weight in 10ml volumetric flask (mg)
n-hexadecane	0.98
pristane	1.084
n-heptadecane	1.00
n-octadecane	1.02
n-docosane	0.98
n-octacosane	1.02
n-dotriacontane	1.02
methyl myristate	1.096
methyl oleate	0.94
methyl linoleate	1.156
total	10.3

A 0.5μl injection (2-5% reproducibility) was made which contained 0.000515 mg of standard solution. This was used to calibrate Chromatochart. Peaks from the G.C. analysis were then quantified on the basis of the G.C. response to the standard mixture.

In certain lipid fractions small spillages occurred. Where possible these have been accounted for. However, the most important conclusions in this report concerning quantifications of fractions are drawn from the ratios of individual components within lipid fractions. Quantification of components relative to other similar components within the same fraction are unaffected by any loss of

that fraction or lack of reproducibility in the amount injected.

Chapter 5 Results

5.1. Core Location

The location of all cores is illustrated in Figure 10. The prefix letters M and L.P. are used to indicate the type of sediment sampler used. M for the Mini-Mackereth Corer and L.P. for the "box freezer" and "icy finger" corers. The sediment examined in this thesis was obtained from two locations. The "head of the neck" (site H) and the area of open water below the southern jetty and midway between the west and east banks (site A).

5.2 Sediment Stratigraphy

Each core was photographed prior to slicing and analysis. The cores are illustrated (Figs. 35-37) and the main stratigraphic units, their depths and probable period of deposition are described in sections 5.2.1-5.2.3. The dates were assigned according to information presented by Coard (in prep.), this was outlined in section 2.3. Fine detail and colour of the sediment cores are shown in the infrared black and white and colour photographs (Plates 1-7).

5.2.1. Core L.P.6

Core L.P. 6 was sampled from site H (Fig. 10), using the box

freezer corer. The stratigraphy is illustrated in Figure 35 and Plates 1 & 2. The core consists of three main sections:

1) 0-36cm   Brown laminated sediment containing a series of light brown, dark brown and black laminated clays. There are approximately 20 discernable laminations.

2) 36-53cm   Laminated pink/black clays with 4 pairs of pink and black varves which each contain a series of microlaminations.

3) 53-66cm   Grey clay with some darker layers but no apparent regular laminations.

Prior to sampling, the core was sliced vertically to facilitate handling. One half of the core was then analysed for the properties of dry weight (section 4.4.2), loss on ignition (section 4.4.2) and pigment content (section 4.4.7). The other half was examined for magnetic variables (section 4.4.3). The core was subsampled for analysis by cutting out the individual laminations. The size of each section varied because of the irregular nature of the laminations. Usually sections were between 0.5 and 2.0 cm thick. The precise stratigraphy of the core, detailing lamination depth and colour is shown in Figure 35. The dates assigned to each core are based on information from Coard (in prep.). The results of properties examined are presented in horizontal bar graphs. For example in Figure 38 the dry weight of L.P. 6 is shown. In these diagrams the depths have been excluded and the thickness of each lamination normalised to a standard size. The colour of each lamination has been indicated. This is to enable comparison of each chemical or physical property with the lamination colour.

Plate 1. Colour photograph of Core L.P.6.
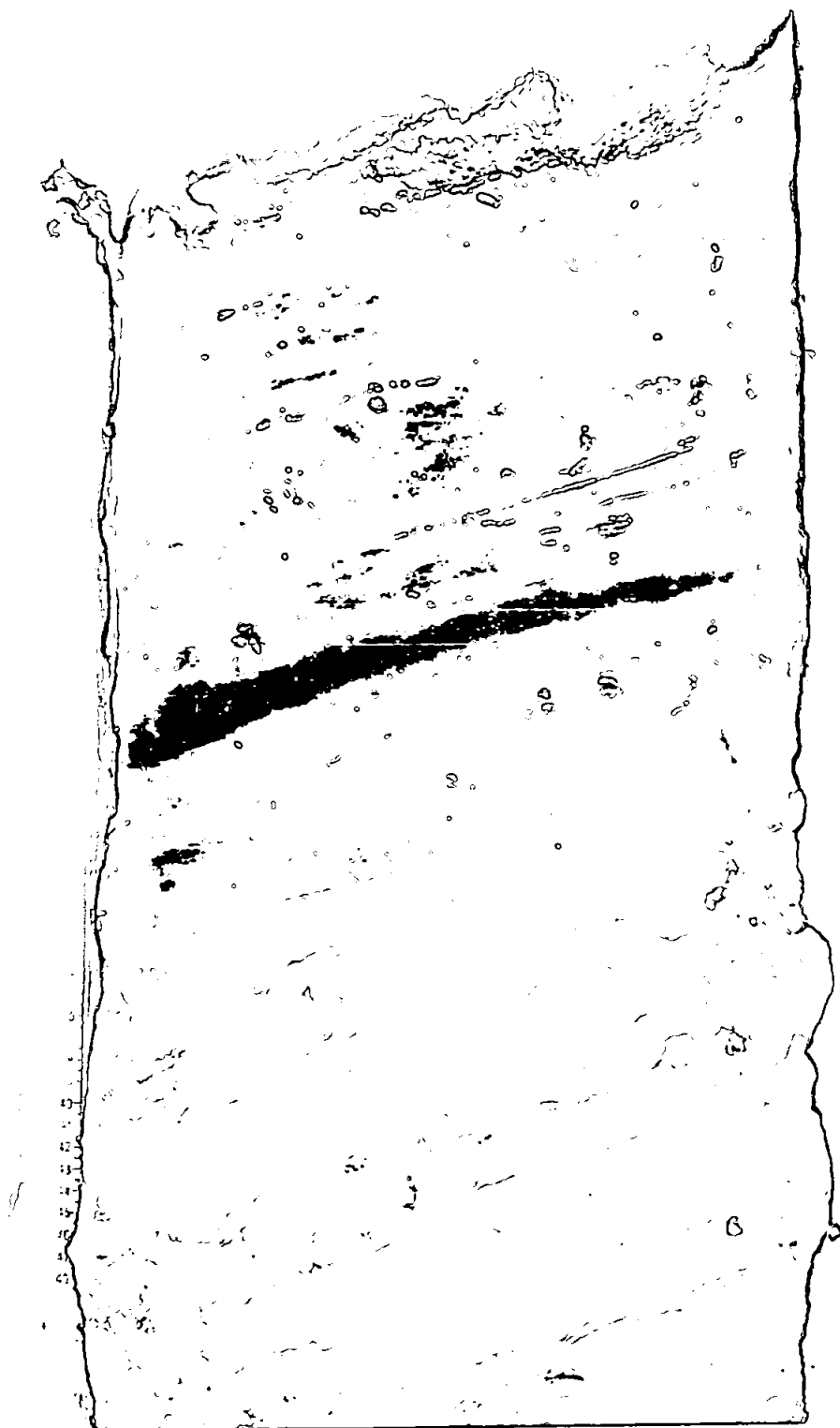
Plate 2. Black & white infra-red photograph of Core L.P.6.
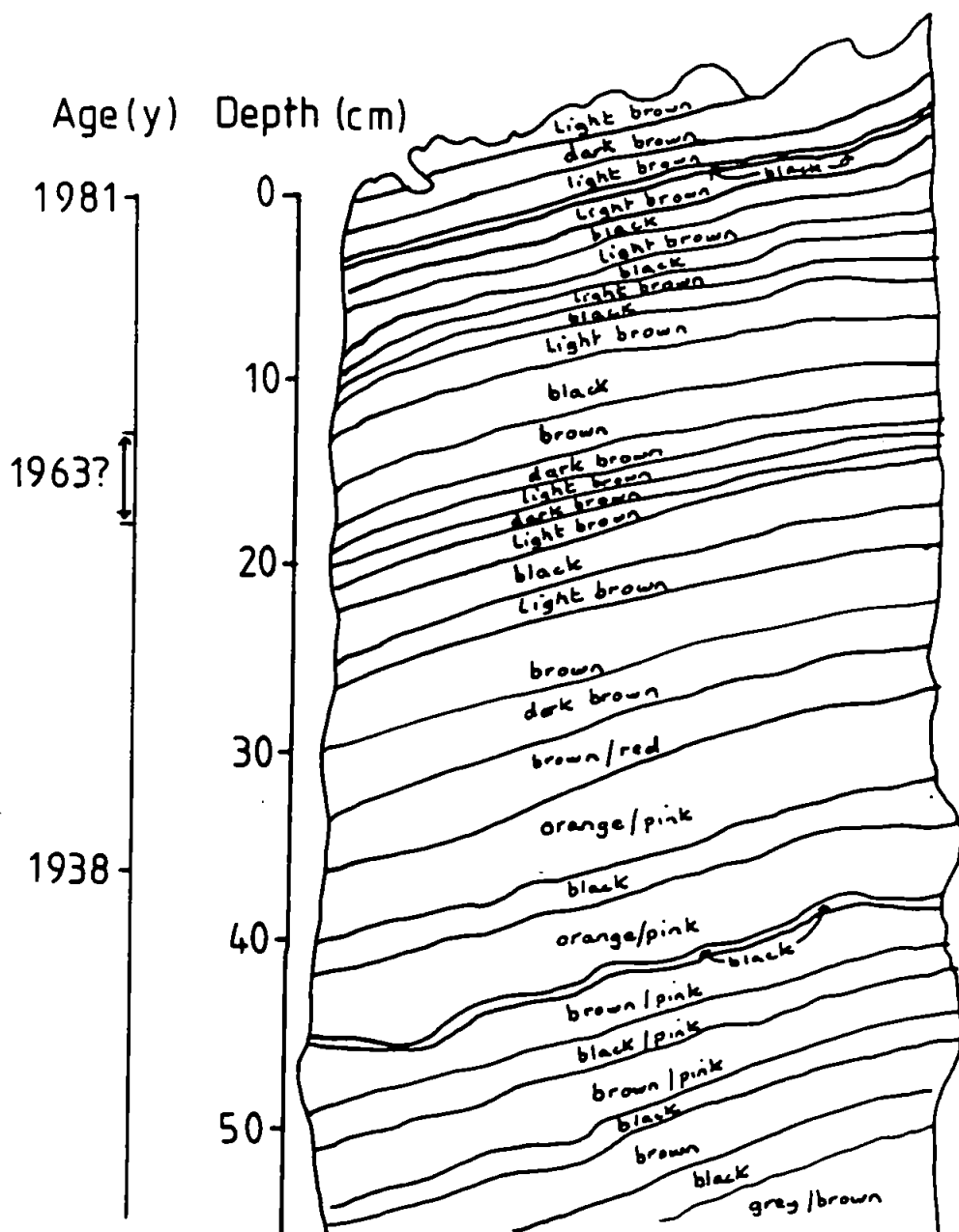
Figure 35. Stratigraphy of Core L.P.6 showing lamination
colours and approximate age with depth of sediment.

5.2.2 Core M1

The Mini-Mackereth core M1, was taken from site A and the stratigraphy is illustrated in Figure 36. The core contains four units of sediment:

1) 0-23.5cm   Brown clay gyttja

2) 23.5-31cm   Pink laminated clay

3) 31-45.6 cm   Grey clay

4) 45.6-90 cm   Black/grey laminated clay.

It was not possible to see any more detail of the stratigraphy because of the limitations of this coring technique (section 4.3.1). The sediment was sliced into 0.67cm sections irrespective of laminations present, and prepared for analysis of magnetic variables (section 4.4.3). Results are presented as horizontal bar charts.

5.2.3 Cores L.P.25, L.P.31, L.P.32 and L.P.35

These cores were collected using the "icy finger" from site A (Fig. 10). Each core had a similar stratigraphy, though the precise depth of laminations deposited at the same time, varied. This stratigraphy is represented in a generalised form for all the cores with precise depths given for L.P.32 (Fig. 37). Each core contains a series of regular black and grey laminations, interrupted by the occurrence of one thick and two thinner pink layers (Plates 3-7).

Initial   investigations   of   the   seasonal   laminations were made with sediment sliced from core L.P.25. One black and one

- 141 -
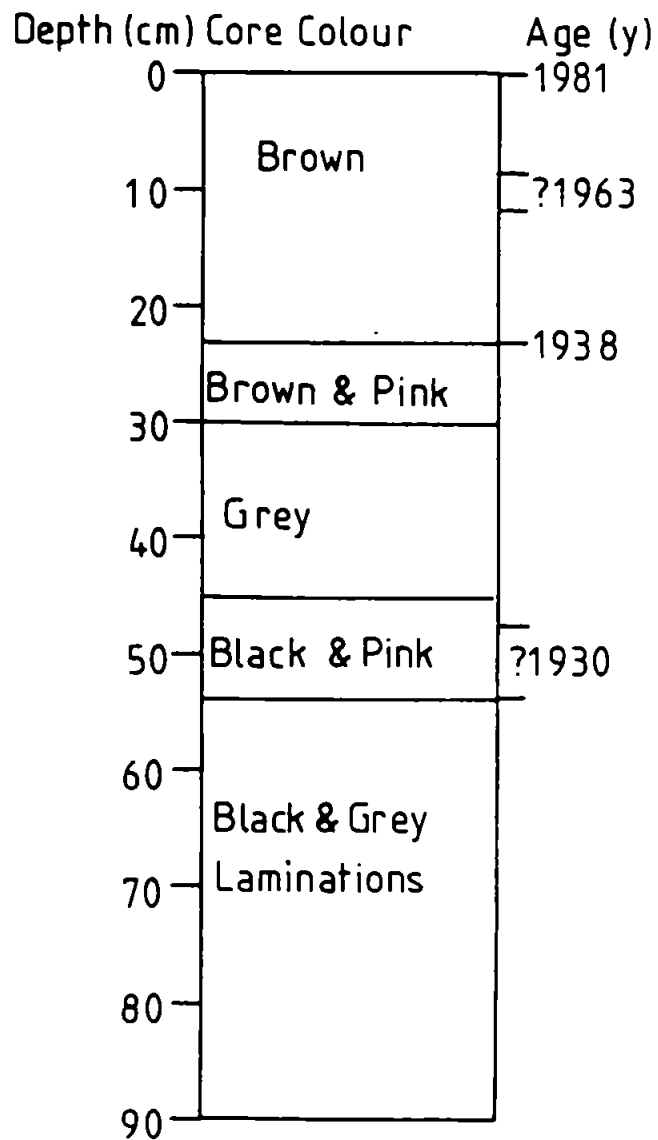
Figure 36. Stratigraphy of Core M1.
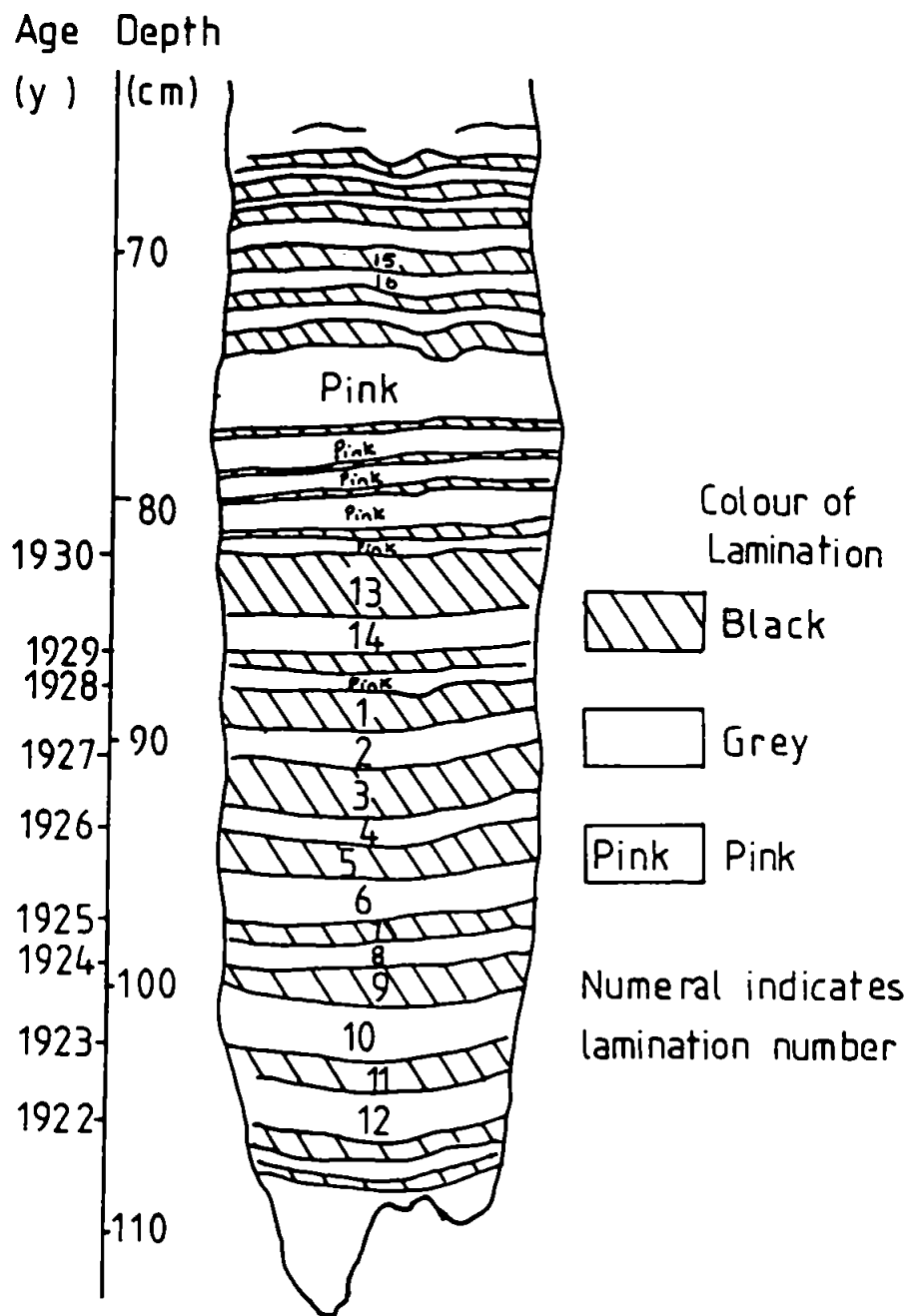
Figure 37. Stratigraphy of Core L.P.32 showing laminations sliced for analysis from the core.

Plate 3. Colour photograph of Core L.P.25.

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Plate 4. Colour photograph of Core L.P.31.

Plate 5. Colour photograph of Core L.P.32.

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grey layer were cut from the depths:

Black lamination   77.5-78.5 cm

Grey lamination   79-80 cm   (Plate 3)

These were designated lamination 1 and 2 respectively.

The sediment is thought to have been deposited in the period c. 1928 (Coard pers. comm.). Evidence presented by Simola et al. (1981) from sediment obtained at the same site and examined at a similar depth indicated that the black and grey couplets made up an annual lamination. Fossil diatom evidence showed that the black and grey layers were deposited in the summer and winter seasons respectively. The results from initial work on core L.P.25 (only data on alkyl esters presented in this report) were substantiated and variation between sediment cores investigated by analysis of the black and grey laminations deposited in the same year from 3 cores collected at the same site. The layers sampled were labelled lamination 1 (black colour/summer deposition) and lamination 2 (grey colour/winter deposition) and were sliced from cores L.P.31, L.P.32 and L.P.35. These were sectioned from the following depths:

Core	Sediment depth (cm)	
L.P.31 lamination 1	86.5-87	(Plate 4)
lamination 2	87-88	
L.P.32 lamination 1	88-89	(Fig. 37 & Plates 5 & 6)
lamination 2	89-90.5	
L.P.35 lamination 1	88-88.5	(Plate 7)
lamination 2	89-90	

In addition properties of a sequence of varves were examined from sediment deposited over a period of approximately 11 years. These were all subsampled from core L.P.32 (Fig. 37 & Plates 5 & 6):

Lamination analysed from core L.P.32	Sediment depth (cm)	Approximate time of deposition
15 (black)	70-71	1933
16 (grey)	71-72	
13 (black)	82.5-85	1930
14 (grey)	85-86	
1 (black)	88-89	1928
2 (grey)	89-90.5	
3 (black)	91-93	1927
4 (grey)	93-94	
5 (black)	94-96	1926
6 (grey)	96-97.5	
7 (black)	97.5-98	1925
8 (grey)	98-99	
9 (black)	99-101	1924
10 (grey)	101-103.5	
11 (black)	103.5-106.5	1923
12 (grey)	106.110	

Plate 6. Black & white infra-red photograph of Core L.P.32.

Plate 7. Colour photograph of Core L.P.35.

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The results of variables examined are presented in the form of horizontal bar charts (for example Fig. 39), with each couplet forming one year's sediment deposition drawn together. The most recently deposited sediment is at the top of the diagrams (L.P.32 lams. 15 & 16) and the earliest at the bottom (L.P. 32 lams. 11 & 12). The sediment from L.P.31 lams. 1 & 2, L.P.32 lams. 1 & 2 and L.P.35 lams. 1 & 2 was deposited in the same year. The close correspondence of laminations between cores is clear from comparison of the photographs (Plates 3-7). Not all physical and chemical properties tested were applied to each lamination because of limitations of time and quantity of sediment available.

5.3 Physical Characteristics of Loe Pool Sediment

5.3.1. Dry Weight of Core L.P.6

The dry weight of L.P.6 is illustrated in Figure 38, the method had a coefficient of variation (C. of V.) of 3.7%. The range of dry weight is from approximately 55% in the red laminated clay to less than 10% at the top of the sediment core. The general trend is an increase in dry weight with depth.

5.3.2 Dry Weight of Cores L.P.31, L.P.32 and L.P.35

The dry weight of the black/grey laminations are shown in Figure 39. The range is from approxiately 27% to 47%, which suggests that

Dry Weight in Loe Pool Sediment
Core LP6
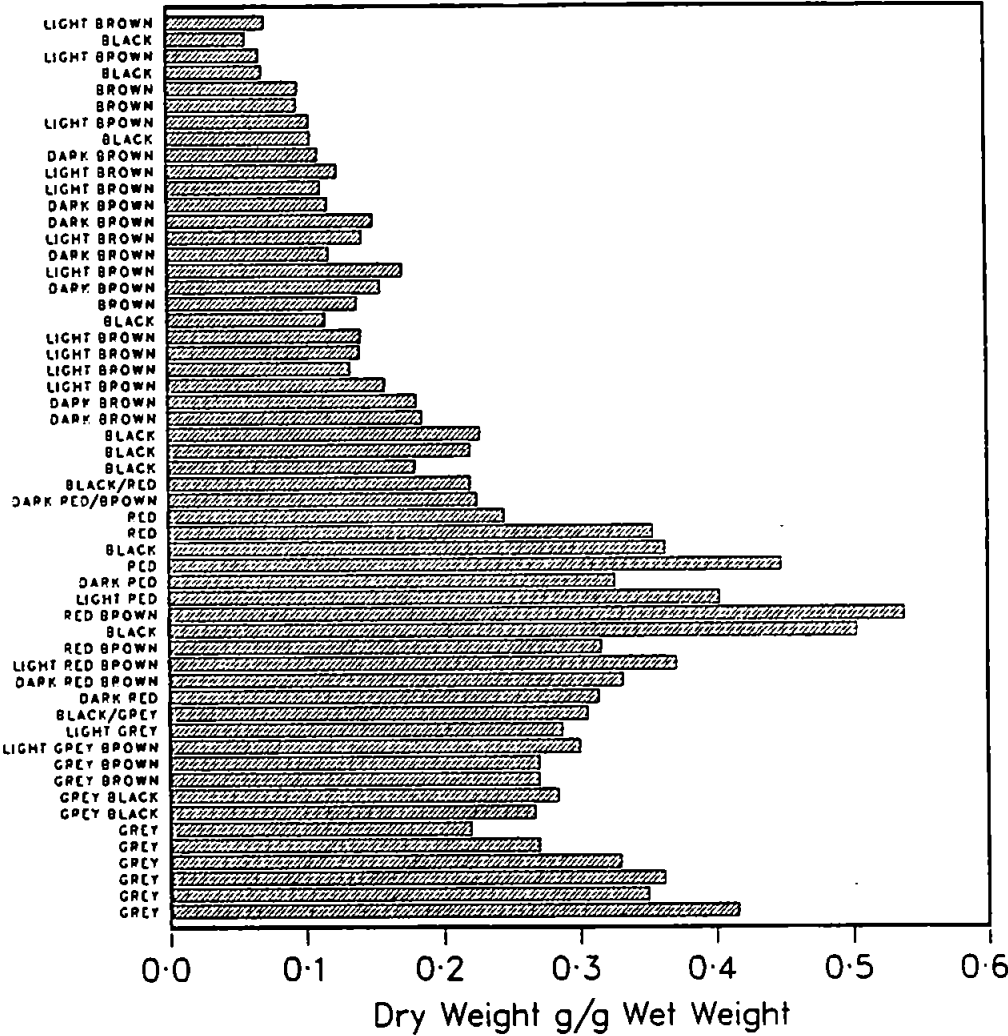
Figure 38. Profile of Dry weight in Core L.P.6 from Loe Pool.

Dry Weight in Loe Pool Sediment

Black Lamination   Grey Lamination
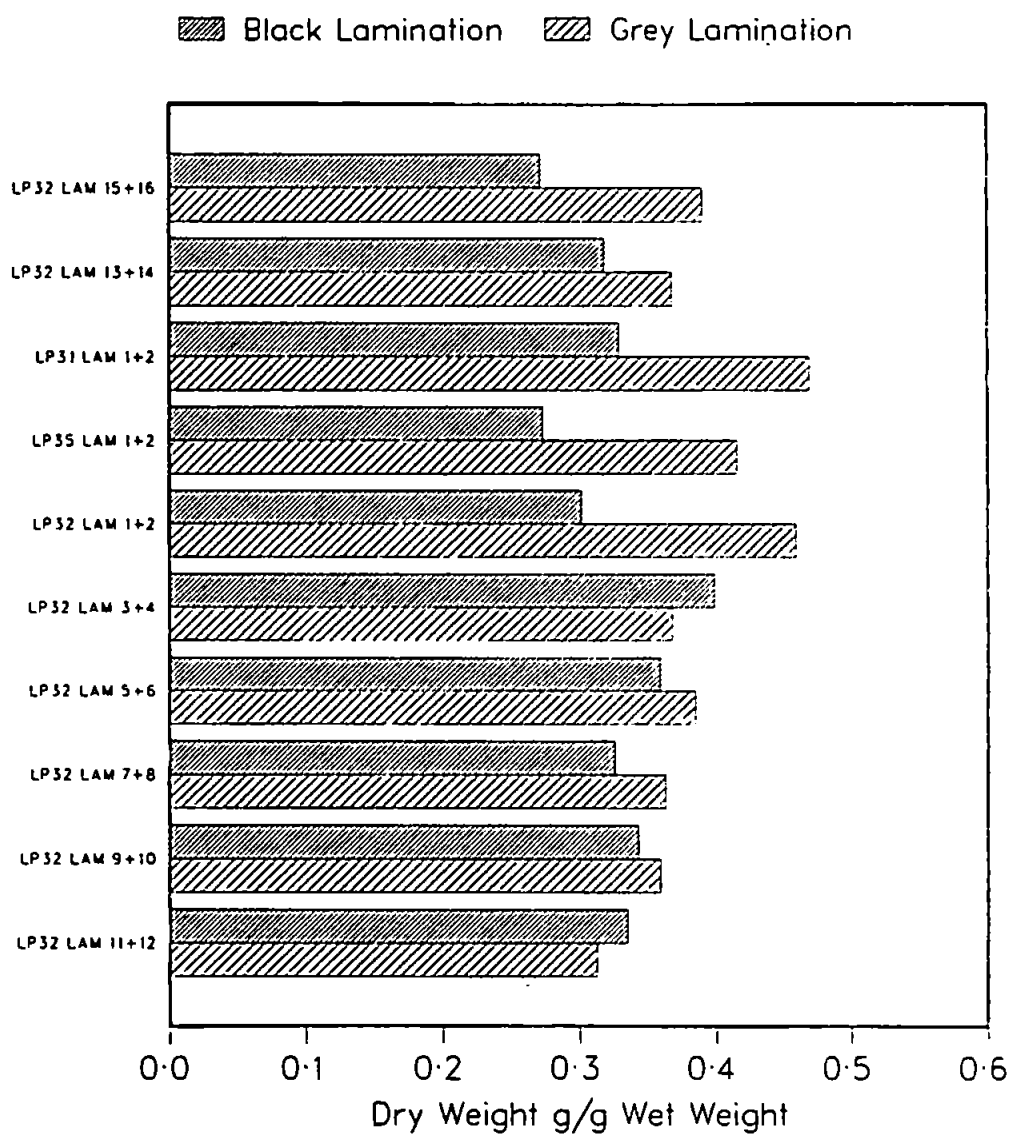
Figure 39. Profile of Dry weight in annual laminations
from cores L.P.31,32 and 35 from Loe Pool.

the general trend of increasing dry weight with depth observed in core L.P.6 continues in the black/grey laminated sediment. It appears that there is a seasonal bias in the dry weight of sediment. Eight of the varves have a higher % dry weight in the grey (winter) than the black (summer) layers. Only six couplets have this relationship ± 1 C. of V., and four ± 2 C. of V.

5.3.3 Loss on Ignition in Core L.P.6

The loss on ignition (L.O.I.) for laminations sampled from core L.P.6 is shown in Figure 40. The C. of V. of the technique is 2.8%. The sediment contains between 3 and 28 % ignitable material. Minimum values occur in the period of massive red clay deposition when the mining activity was particularly intense in the catchment area. The general trend in the sediment stratigraphy is for an increase in L.O.I. from the base to the top of the core. There are few consistent differences between the different coloured laminations. However, higher values of L.O.I. tend to occur in the black or dark brown and lower values in the light coloured sediment.

5.3.4 Loss on Ignition in Cores L.P.31, L.P.32 and L.P.35

The L.O.I. of the black and grey varved sediment is illustrated in Figure 41. The range of L.O.I. is from 0.02-0.1 g/g dry weight. Lower values occur in the upper part of the sediment stratigraphy. Seven of the couplets have a higher L.O.I. value in the black (summer) than the grey (winter) laminations. Five couplets exhibit

Loss on Ignition in Loe Pool Sediment
Core LP6

Loss on Ignition g/g Dry Weight
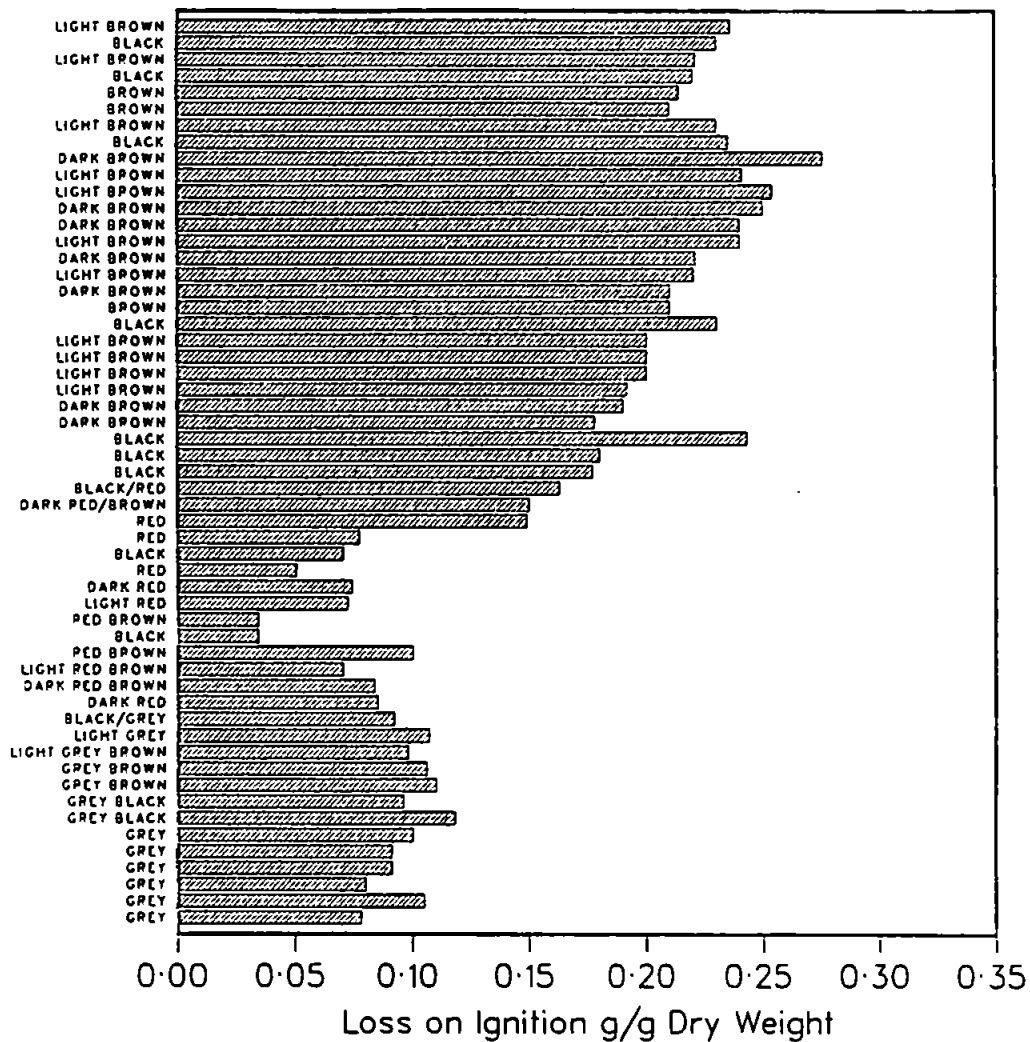
Figure 40. Profile of Loss on Ignition in Core L.P.6
from Loe Pool.

Loss on Ignition in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
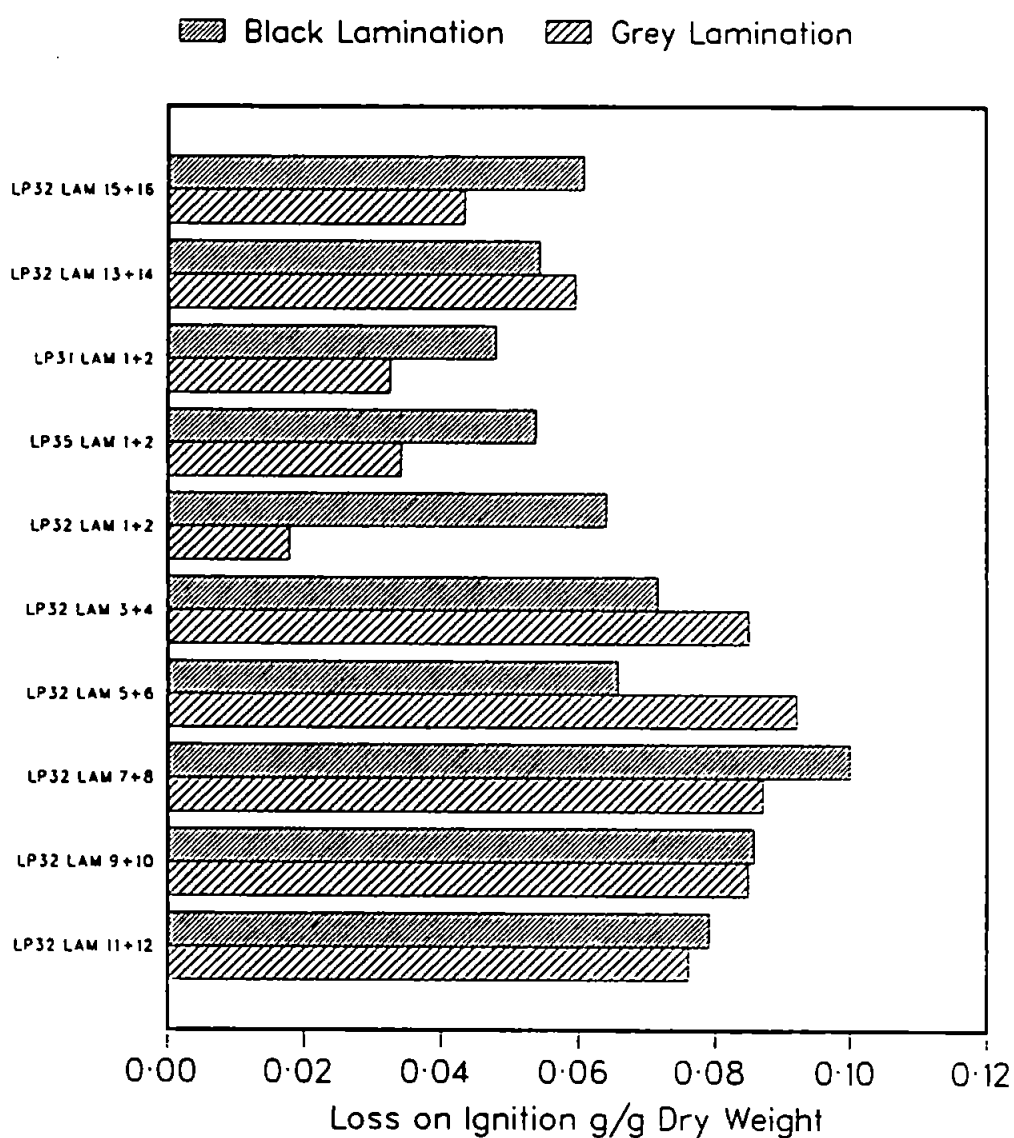
Figure 41. Profile of Loss on Ignition in annual laminations
from Cores L.P.31,32 and 35 from Loe Pool.

this variation with $\pm$ 2 C. of V.

5.3.5 Combustion Residue in Core L.P. 6

The combustion residue (C.R.) in core L.P.6 is illustrated in Figure 42, the method had a C. of V. of 0.36%. The C.R. varies between approximately 72% and 97% of the dry weight of each sample. Highest values occur in the sediment deposited at the time of peak mining activity. There is a general trend from the cessation of mining to the present day of a gradual reduction in the proportion of C.R. There are no discernable differences between C.R. value and colour of lamination.

5.3.6 Combustion Residue in Cores L.P.31, L.P.32 and L.P.35

The range of C.R. in the black/grey laminated sediment is from 90% to 98% dry weight, this is illustrated in Figure 43. As with the property of dry weight, the highest values in the black/grey sediment sequence occur at the top of the sediment stratigraphy. There does not appear to be a strong seasonal bias in the distribution of C.R. Seven of the winter laminations have a higher % C.R. than their respective summer laminations. This trend is consistent in five varves $\pm$ 1 C. of V. and in four varves $\pm$ 2 C. of V.

Combustion Residue in Loe Pool Sediment Core LP6
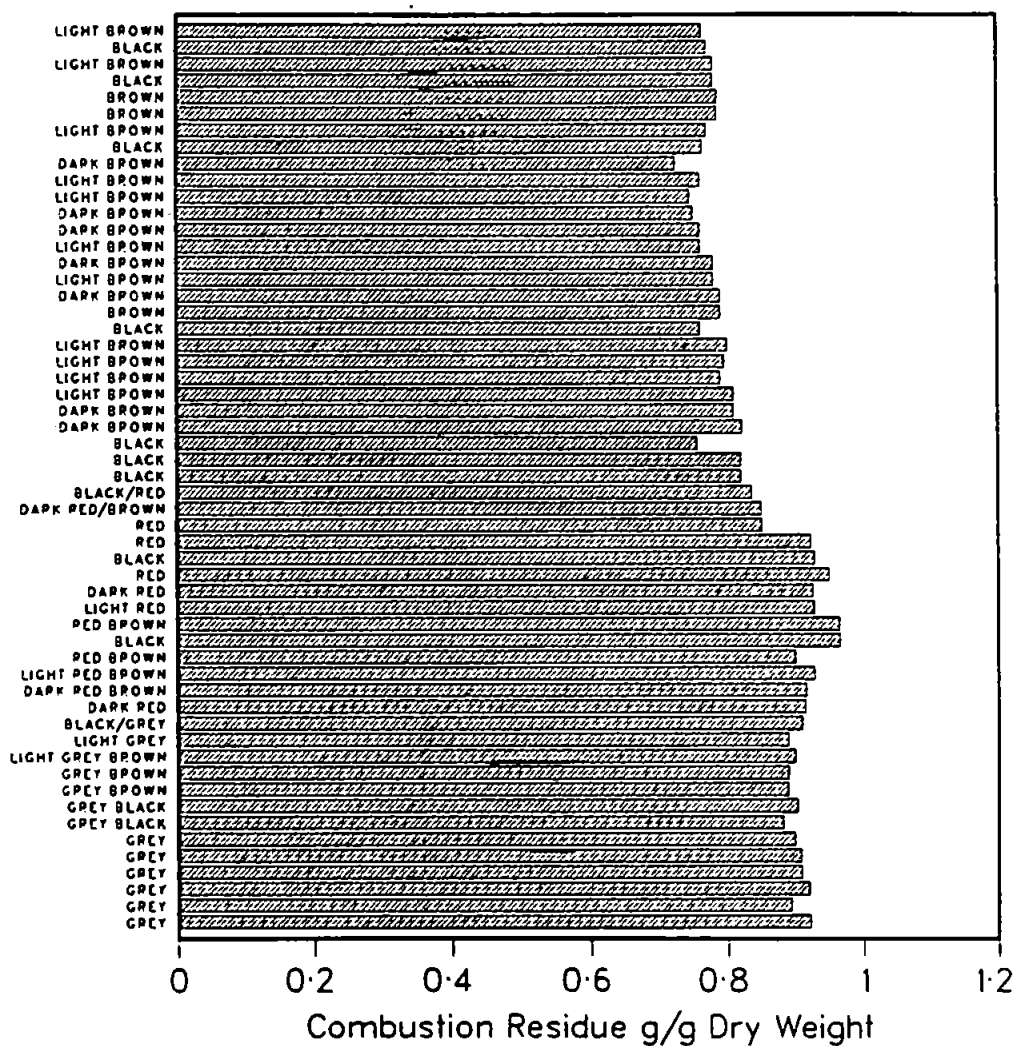
Figure 42. Profile of Combustion Residue in Core L.P.6 from Loe Pool.

Combustion Residue in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
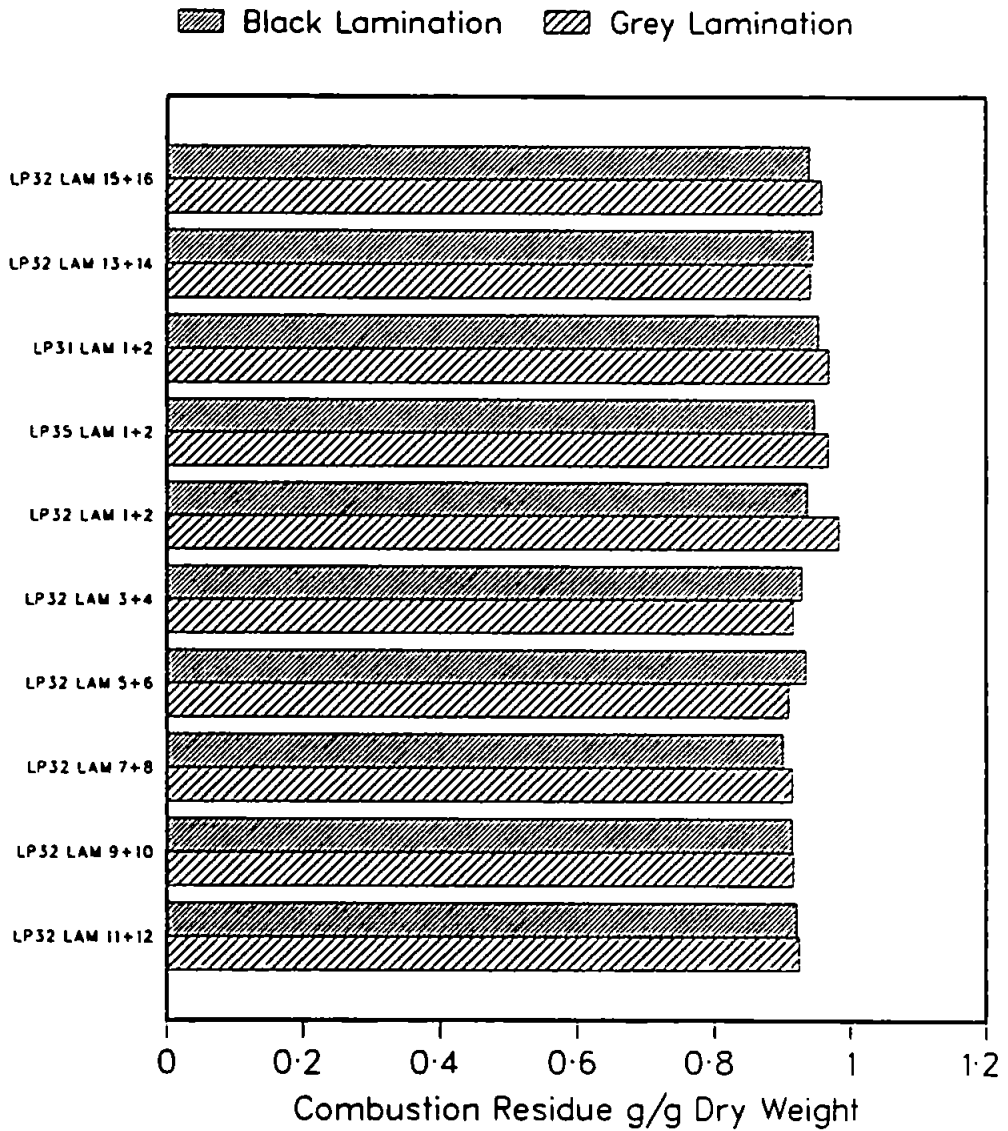
Figure 43. Profile of Combustion Residue in annual laminations from Cores L.P.31,32 and 35 from Loe Pool.

5.4 Magnetic Variables

Three cores from Loe Pool were analysed for selected magnetic variables, details are shown in Table 11. Core M1 was sliced at 0.67cm intervals and L.P.6 and L.P.32 were cut to remove individual laminations as described in section 5.2.1, 5.2.2 and 5.2.3. Each variable measured is presented in a horizontal bar chart. The major stratigraphic sedimentary unit and, where appropriate, the colour of individual laminations are indicated. A blank container was included for each analytical procedure, there was no detectable response for any of the magnetic variables measured from it. No details of the magnetic properties of sediment from L.P.31 lams. 1 & 2, L.P.32 lams. 1 & 2 and L.P.35 lams. 1 and 2 are available because of insufficient material.

5.4.1 Magnetic Susceptibility

The magnetic susceptibility of cores analysed is presented in Figures 44-46. Variation of susceptibility between the different stratigraphic units is best seen in core M1 (Fig. 45). The range of magnetic susceptibility for this core is shown in Table 12.

Core L.P.6 collected from site H has slightly higher magnetic susceptibility values in the red/black laminated clay than the brown clay gyttja unit (Fig 44). The susceptibility values of the black/grey laminations from core L.P.32 (Fig. 46) have a similar range as the corresponding sediment in M1 (Fig. 45). Both cores M1 and L.P.32 were collected from site A (Fig. 10).

Magnetic variable analysed from Loe Pool sediment				
Core	Susceptibility	S Ratio	S.I.R.M.	S.I.R.M./Susceptibility
LP6	Yes	No	Yes	Yes
M1	Yes	No	Yes	Yes
LP32	Yes	Yes	Yes	Yes

Table 11. Magnetic Variables Analysed from Loe Pool Sediment.

Sediment Stratigraphy	Sediment depth (cm)	Magnetic Susceptibility $(10^{-6} \text{ G.Oe}^{-1}\text{cm}^{-3}\text{g}^{-1})$
Brown clay gyttja	0-23	7.7-11.4
Pink laminated clay	23-31	3.3-10.0
Grey clay	31-45	6.7-9.0
Black/grey laminations	45-90	2.7-9.2

Table 12. Range of Magnetic Susceptibility in the Sedimentary Units from Core M1.

Susceptibility in Loe Pool Sediment Core LP6
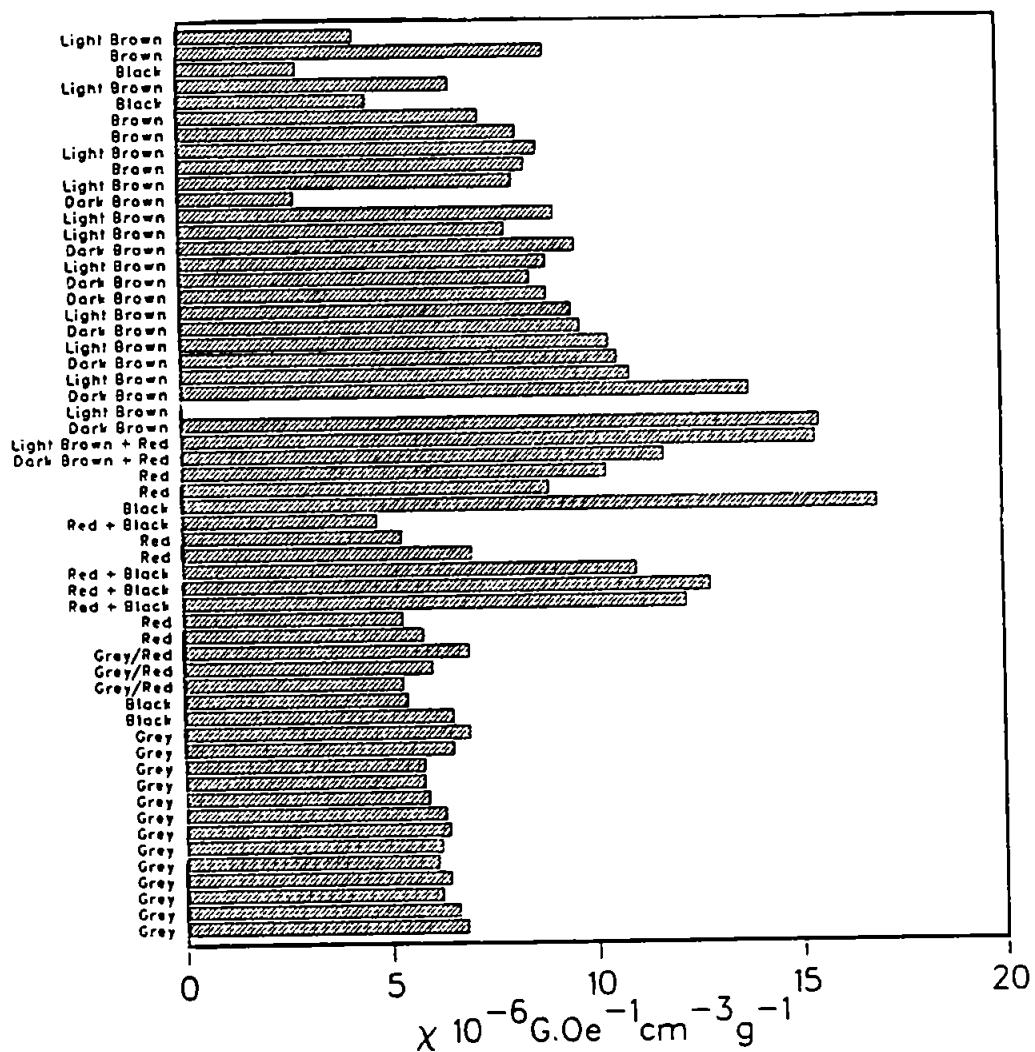
Figure 44. Profile of Magnetic Susceptibility in Core L.P.6 from Loe Pool.
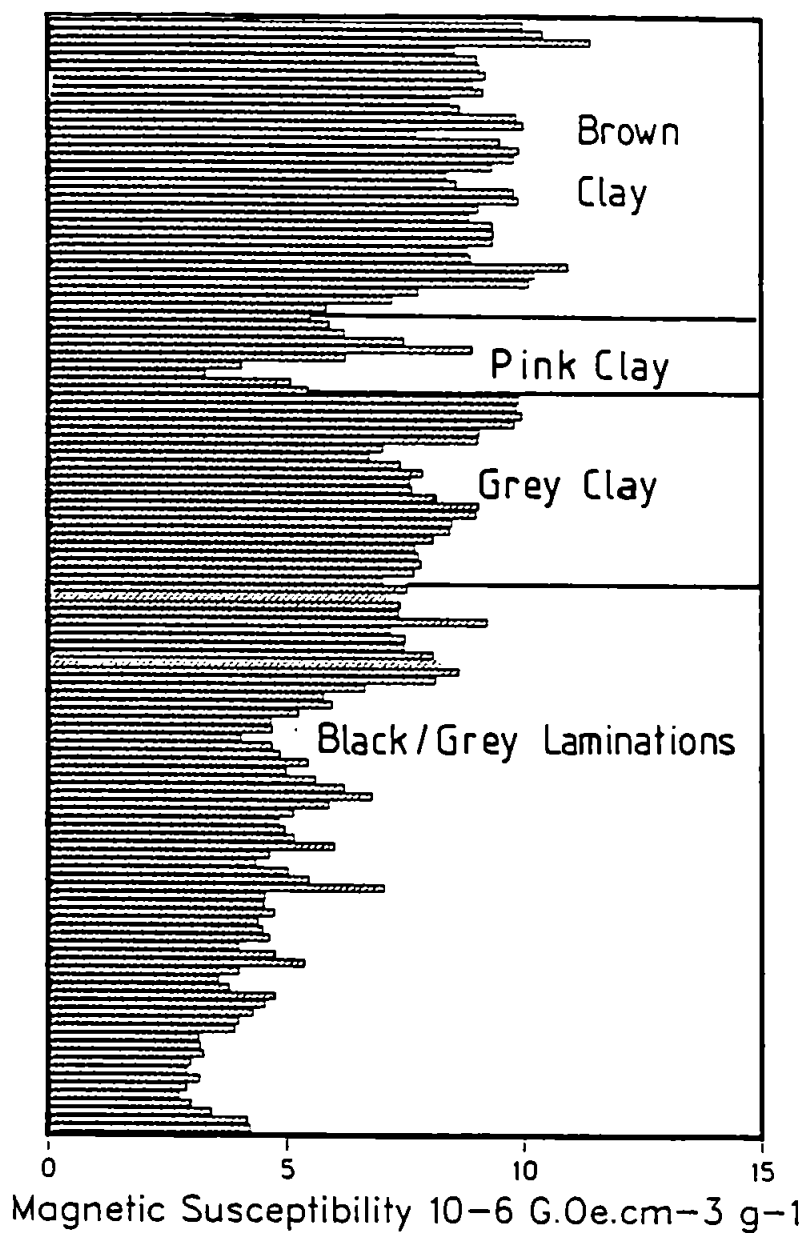
Figure 45. Profile of Magnetic Susceptibility in Core M1 from Loe Pool.

Low Frequency Susceptibility in Loe Pool Sediment

Black Lamination   Grey Lamination
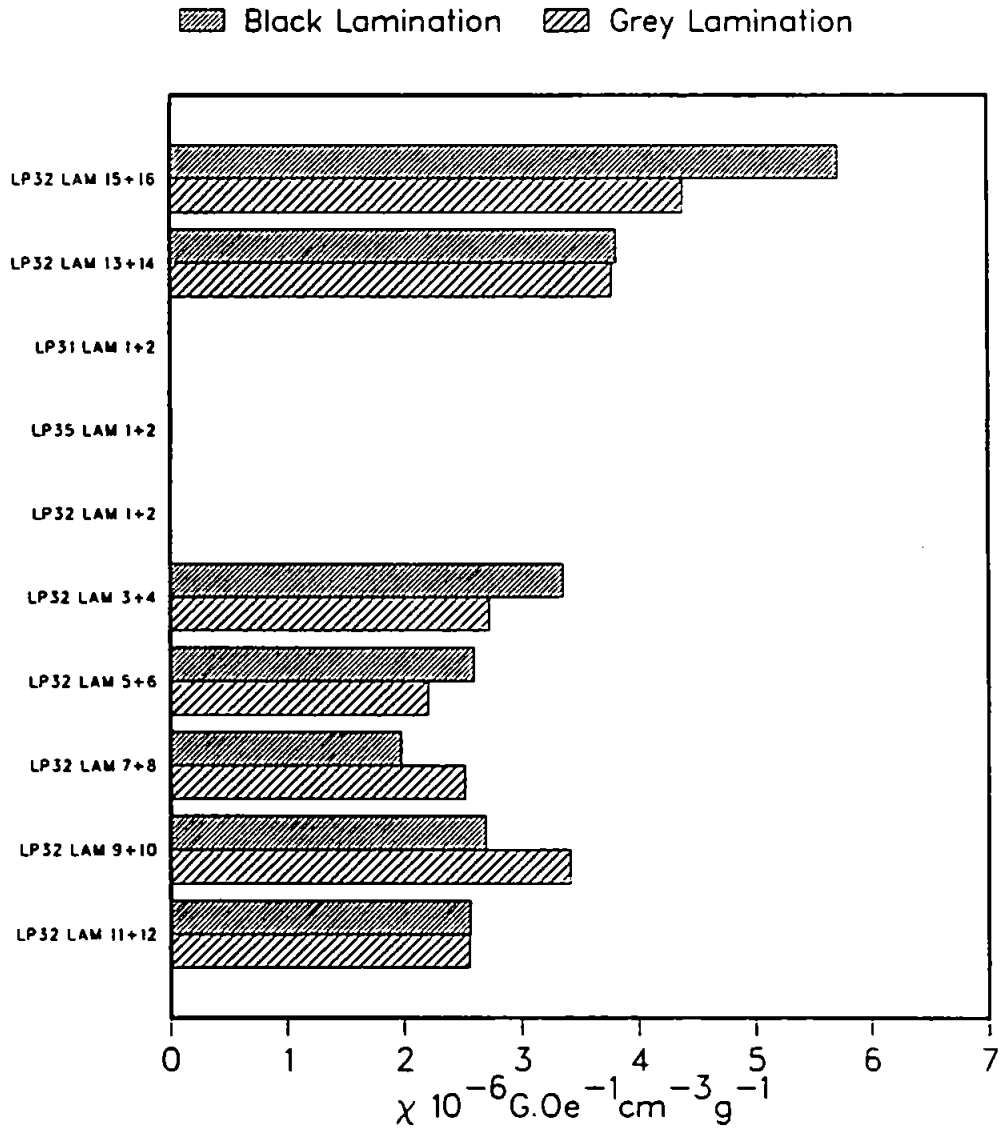
Figure 46. Profile of Low Frequency Magnetic Susceptibility in annual laminations of Core L.P.32 from Loe Pool.

5.4.2 S Ratio

The S ratio was only calculated for the black/grey laminations from core L.P.32. Values vary in the range 4-43 and the data are presented in Figure 47.

5.4.3 Saturated Isothermal Remanent Magnetism

Data from the analysis of Saturated Isothermal Remanent Magnetism (S.I.R.M.) of cores L.P.6, Ml and L.P.32 are presented in Figures 48-50. The ranges of values in each stratigraphic unit in core Ml are shown in Table 13. Each stratigraphic unit deliminated in core Ml is clearly discernable in terms of S.I.R.M. values. The S.I.R.M. of sediment from core L.P.6 had a higher S.I.R.M. range in each of the corresponding stratigraphic units than Ml.

5.4.4 S.I.R.M./Susceptibility

The S.I.R.M./magnetic susceptibility ratio of cores Ml, L.P.6 and L.P.32 are illustrated in figures 51-53. The ratio for Ml exhibits variation in the sedimentary units deposited during the period of most intense mining from 1930-1940. The deeper black/grey laminated sediment has a ratio around 24 ± 4 (with the exception of one anomalous result). In the brown clay present in cores L.P.6 and Ml the ratio again shows little variation, with values of 11.5 ±2.5. The S.I.R.M./ magnetic susceptibility ratio of both Ml and L.P.6 peak in the red/black laminated sediment.

S Ratio in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
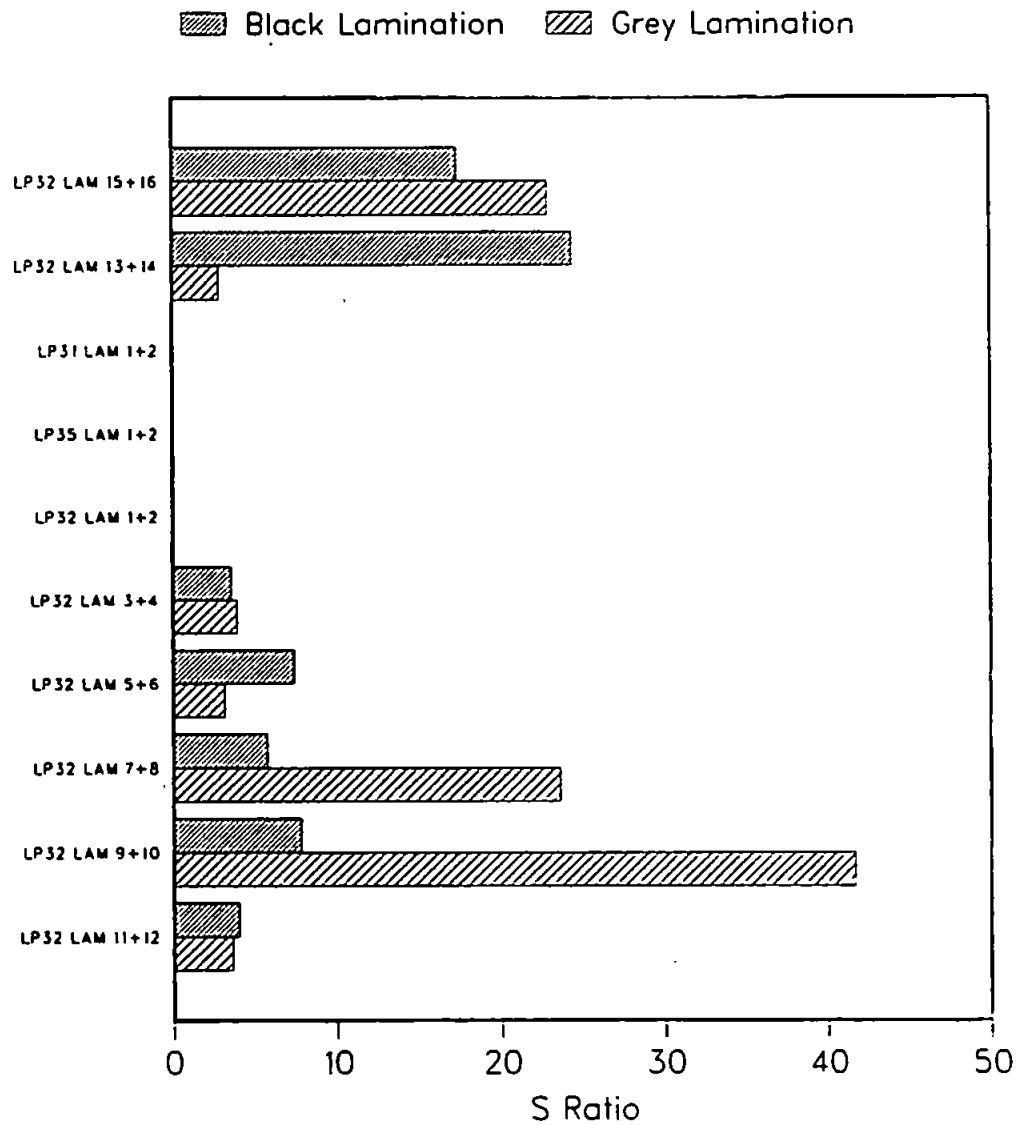
Figure 47. Profile of S Ratio in the annual laminations of
Core L.P.32 from Loe Pool.
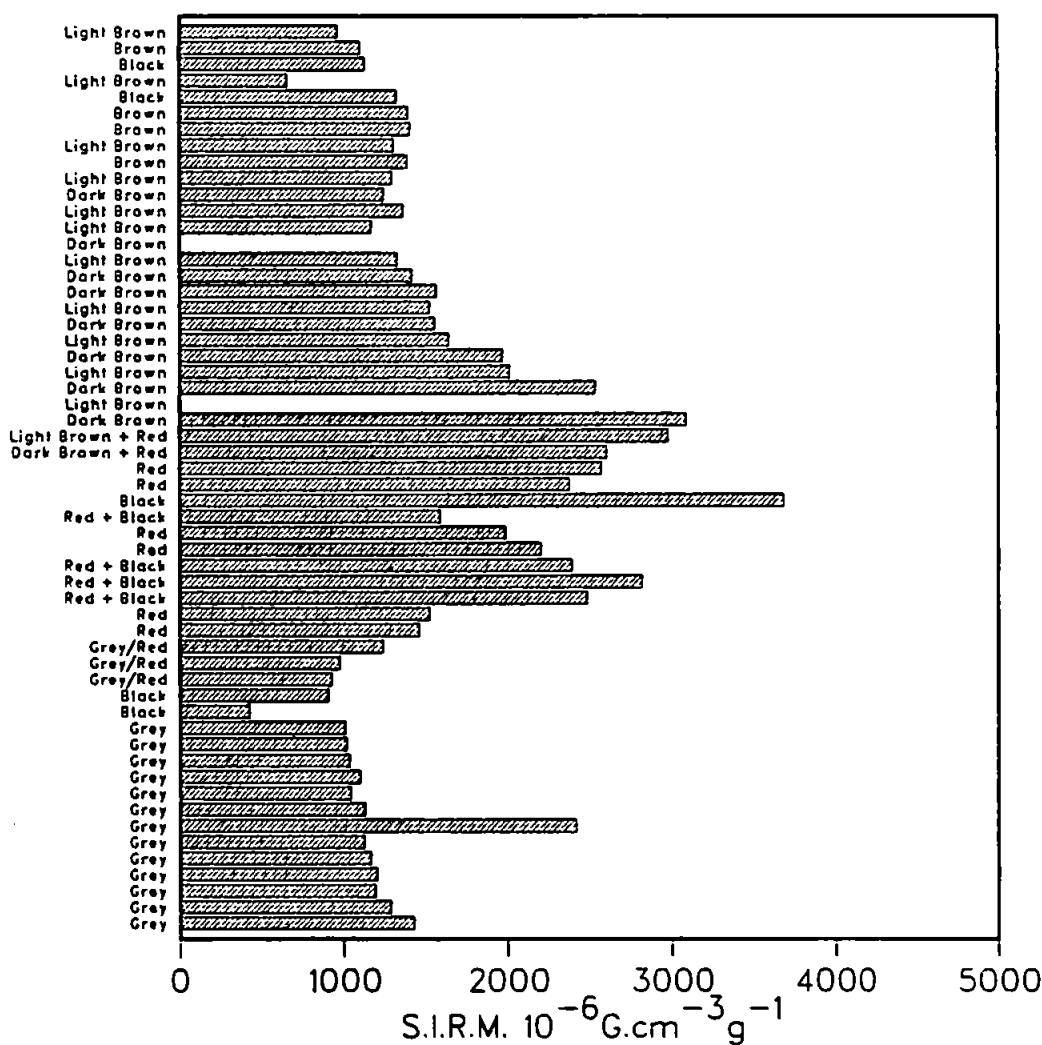
Figure 48. Profile of Saturated Isothermal Remanent Magnetism in Core L.P.6 from Loe Pool.

S.I.R.M. in Loe Pool Sediment
Core M1

Brown Clay

Pink Clay

Grey Clay

Black/Grey

Laminations

S.I.R.M. 10-6 G cm-3 g-1
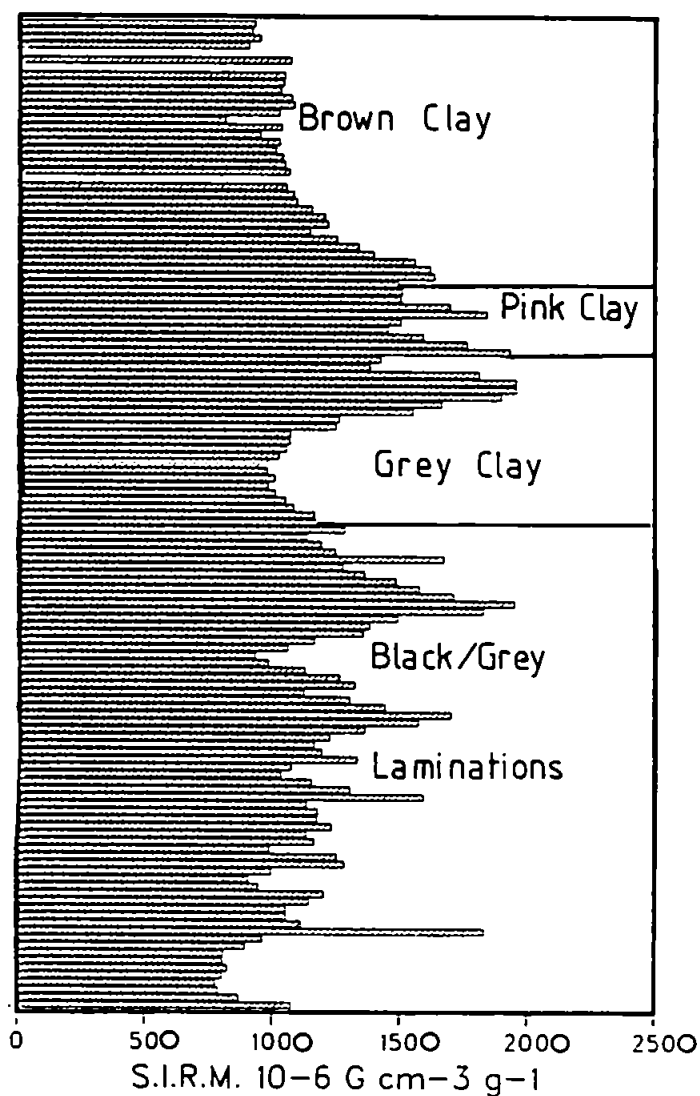
Figure 49. Profile of Saturated Isothermal Remanent
Magnetism in Core M1 from Loe Pool.

S.I.R.M. in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
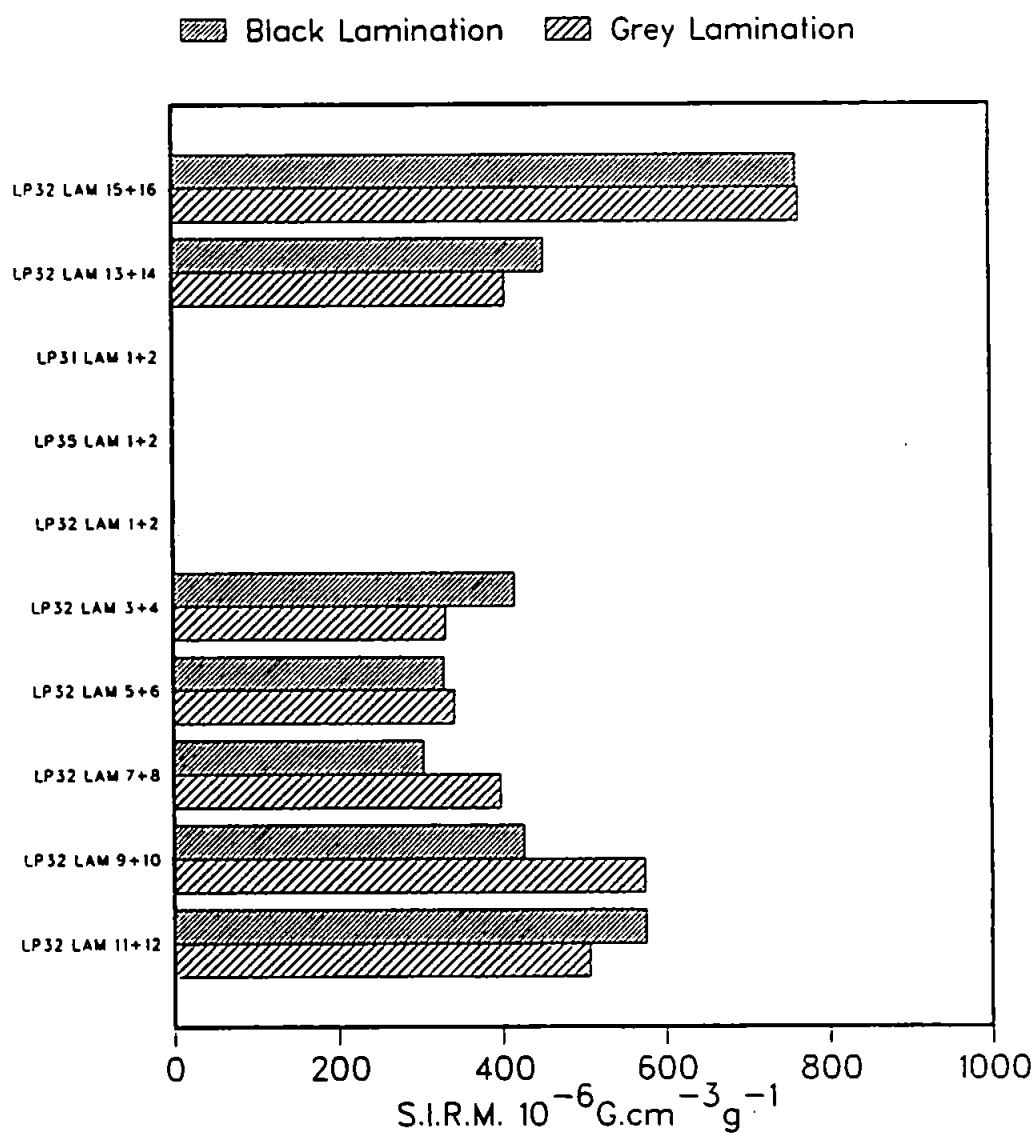
Figure 50. Profile of Saturated Isothermal Remanent
        Magnetism in annual laminations in Core L.P.32
        from Loe Pool.

S.I.R.M : Susceptibility in Loe Pool Sediment Core LP6
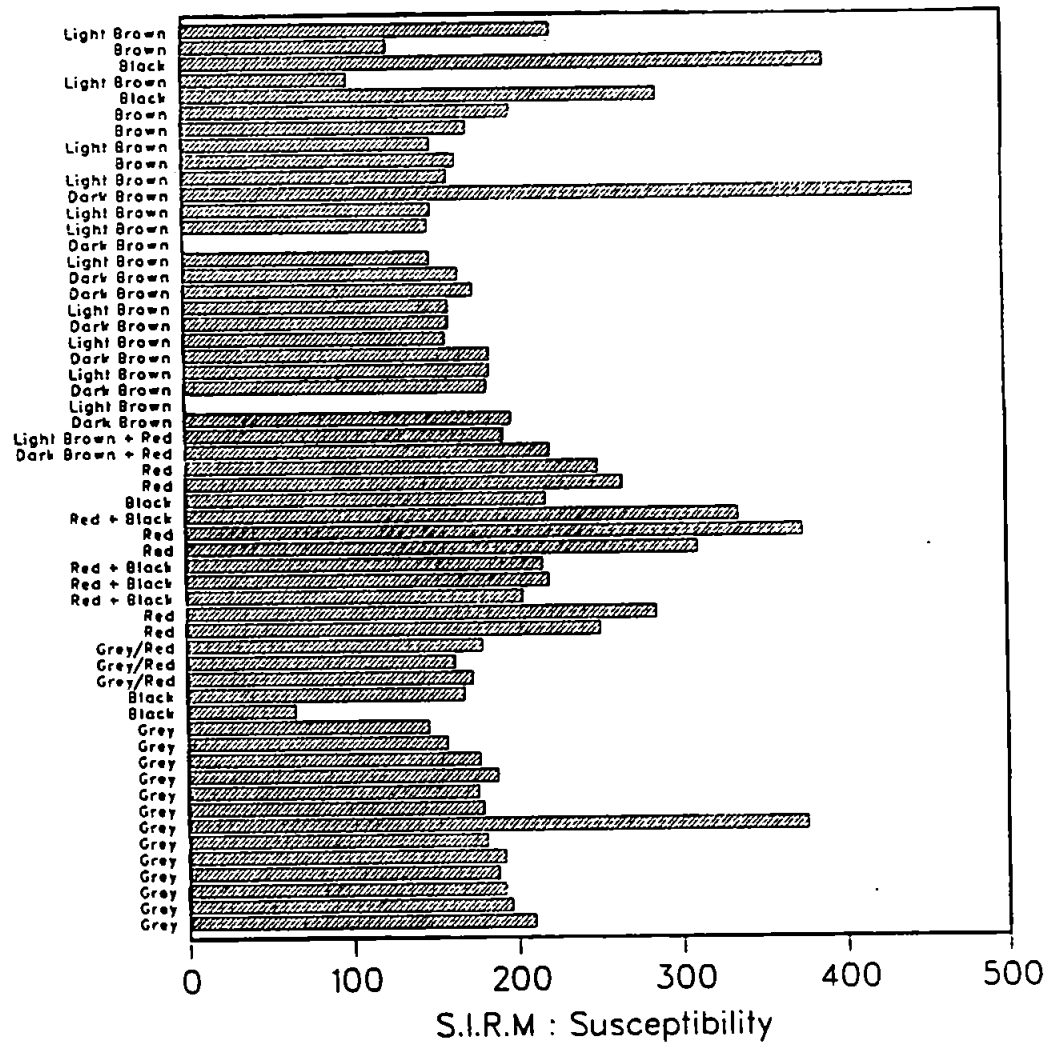
Figure 51. Profile of the ratio of Saturated Isothermal Remanent Magnetism : Magnetic Susceptibility in Core L.P.6 from Loe Pool.

Figure 52. Profile of the ratio of Saturated Isothermal Remanent Magnetism : Magnetic susceptibility in Core M1 from Loe Pool.

S.I.R.M./Low Frequency Susceptibility in Loe Pool Sediment

Black Lamination   Grey Lamination
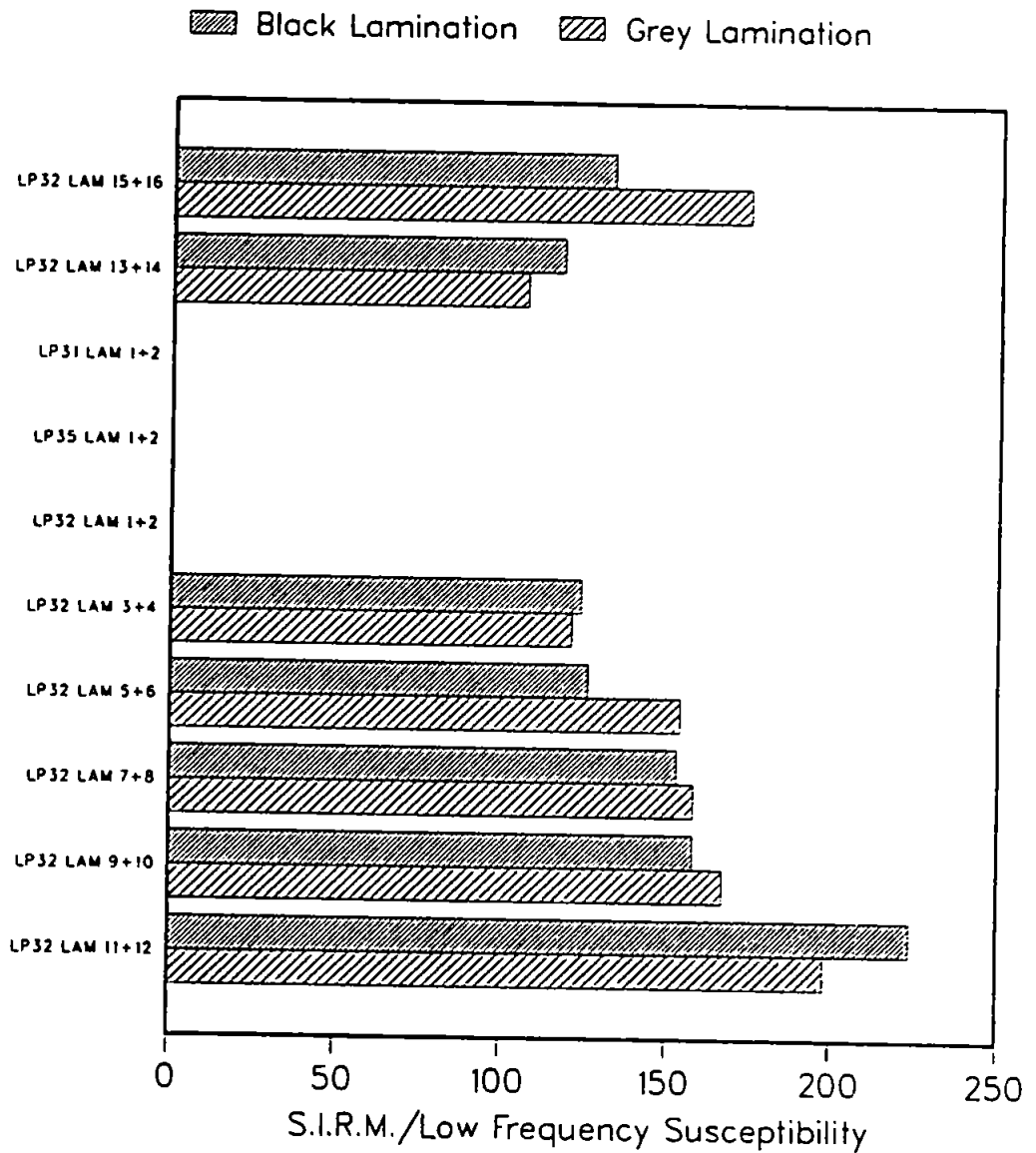
Figure 53. Profile of the ratio of Saturated Isothermal Remanent Magnetism: Magnetic Susceptibility in annual laminations from Core L.P.32 from Loe Pool.

5.4.5 Comparison of Magnetic Variables between Cores

Correlation coefficients of magnetic variables between cores were not calculated. However, visual comparison of the magnetic susceptibility profiles from cores L.P.6 and L.P.32 indicate that a similiar trend is present in each core. This is illustrated in Figure 54, with the major stratigraphic units delimited.

5.4.6 Correlation between Magnetic Susceptibility and S.I.R.M. in
Cores Ml, and L.P. 6

Correlation coefficients between magnetic susceptibility and S.I.R.M. were calculated for the whole cores L.P.6 and M1 and the brown clay gyttja and red/black + grey clay sediment in L.P.6. These are shown in Table 14.

5.4.7 Variations of Magnetic Properties between the Black and Grey
Seasonal Laminations

Seven pairs of black and grey seasonally-deposited laminations from core L.P.32 were investigated for the magnetic variables of susceptibility, S.I.R.M., S ratio and S.I.R.M./susceptibility ratio (Figs. 46, 47, 50 & 53). There were no apparent differences of the variables measured between the black (summer) and grey (winter) laminations.

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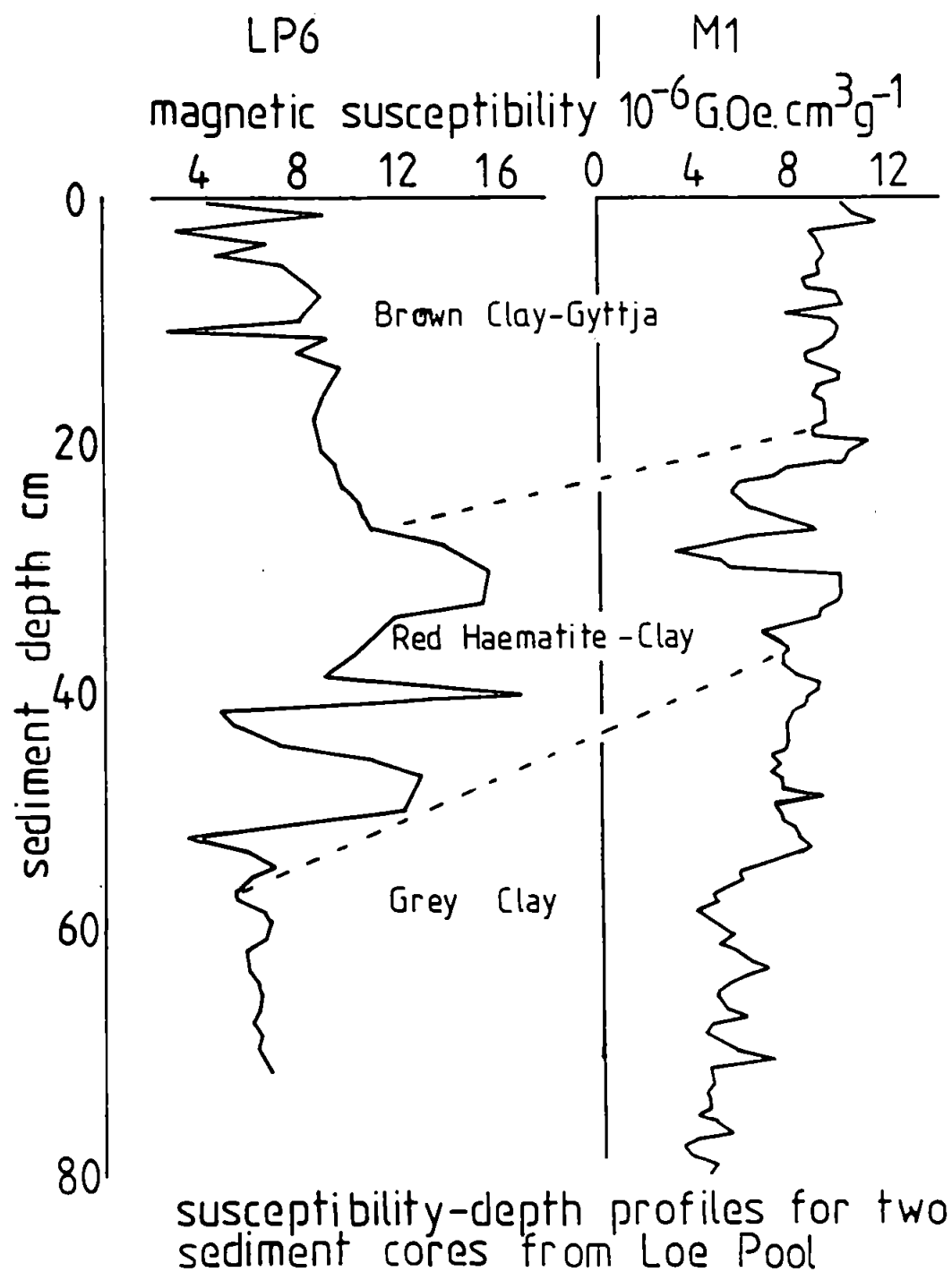
Figure 54. Comparison of Magnetic Susceptibility profiles of Cores L.P.6 and M.1 from Loe Pool.

Sediment Stratigraphy	Sediment depth (cm)	Range of S.I.R.M. 10^{-6} G.cm^{-3}g^{-1}
Brown clay gyttja	0-23	902-1556
Pink laminated clay	23-31	1490-1930
Grey clay	31-45	977-1955
Black/grey laminations	45-90	770-1949

Table 13. Range of Saturated Isothermal Remanent Magnetism in Core M1.

Whole or Section of core	Correlation Coefficients	t
M1 Whole core	+ 0.809	15.8 **
L.P.6 Whole core	+ 0.79	10.55 **
L.P.6 Brown clay gyttja	+ 0.28	2.91 *
L.P.6 Pink/black and grey sediment	+ 0.92	11.73 **

Table 14. Correlation Coefficients between Magnetic Susceptibility and S.I.R.M. in Loe Pool Sediment.

* significant $0.005 < p < 0.001$

** significant $0.001 < p < 0.0005$

5.5 Metals in the Black and Grey Laminated Sediment

The range of concentrations of selected elements analysed in the black/grey laminations formed in Loe Pool are given together with figures for comparison from other sites, in Table 15. It should be noted that the concentrations of the elements analysed from Loe Pool sediment are based on a 'hot extraction' technique (section 4.4.4.1). Many of the concentrations in Table 15 are for 'total' extracts. If the Loe Pool sediment was subject to a 'total' extract, then the concentration of each element would be greater. The concentration of each element is presented in a separate bar chart (for example, Fig. 55). The extraction and analysis of one sample was repeated 5 times in order to calculate the coefficient of variation for each element. A procedural blank did not contain significant concentrations of any of the elements analysed.

5.5.1 Iron

The concentration of iron (Fe) in the individual black and grey seasonal laminations is shown (Fig. 55). The C. of V. was 9.4%. The range of iron in sediment analysed from Loe Pool was 1.5-4.5%. This is less than the crustal average and is in the lower range of the iron concentrations reported in other lake sediments (Table 15). There is an apparent difference in concentration of iron between the seasonal laminations. In eight of the ten couplets there is a higher concentration in the black (summer) than grey (winter)

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Lake	Element Concentration (range or average)											Reference
	Fe (%)	Mn (ppm)	Ni (ppm)	Na (ppt)	Co (ppm)	Pb (ppm)	Ca (%)	Mg (ppt)	Zn (ppm)	Cu (ppm)	K (ppt)	
Loe Pool	1.5-4.5	250-550	10-35	2.5-6.4	15-40	150-320	1-7.5	1-10	360-1500	500-2000	0.8-1.6	This study
Windermere North Basin	5.09-6.23	1457-32966	33-44	6.2-7.3	13-21	161-254			389-499	47-54	16.2-18.4	Rowlatt, 1980
Crust	5.6	950	75	24	25	12.5			70	55	21	Krauskopf, 1967
Average lacustrine deposits	1.2-6.9	100-1800	30-250		3-40	8-75			45-220	20-80		Förstner, 1977
Windermere South Basin	4.91	17280	41	5.7	10	322			586	50	14.6	Rowlatt, 1980
Lake Michigan	2.83	560	34	4.6	13	88			206	37	18.2	Leland et al., 1973
Lake of the Clouds	2.0-12.0	1500-14000										Anthony, 1977
Harveys Lake	5.0-14.0	5000-100000										Engstrom et al., 1985
Range of lake sediments	0.5-2.0	200-3000	5-50	0.2-2	0.2-20	2-100	0.5-2	0.5-20	20-500	5-300	0.5-5	Bengtsson, 1979

Table 15. Comparison of elemental concentrations in Loe Pool with results from other lacustrine sediments and bedrock.

Iron in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
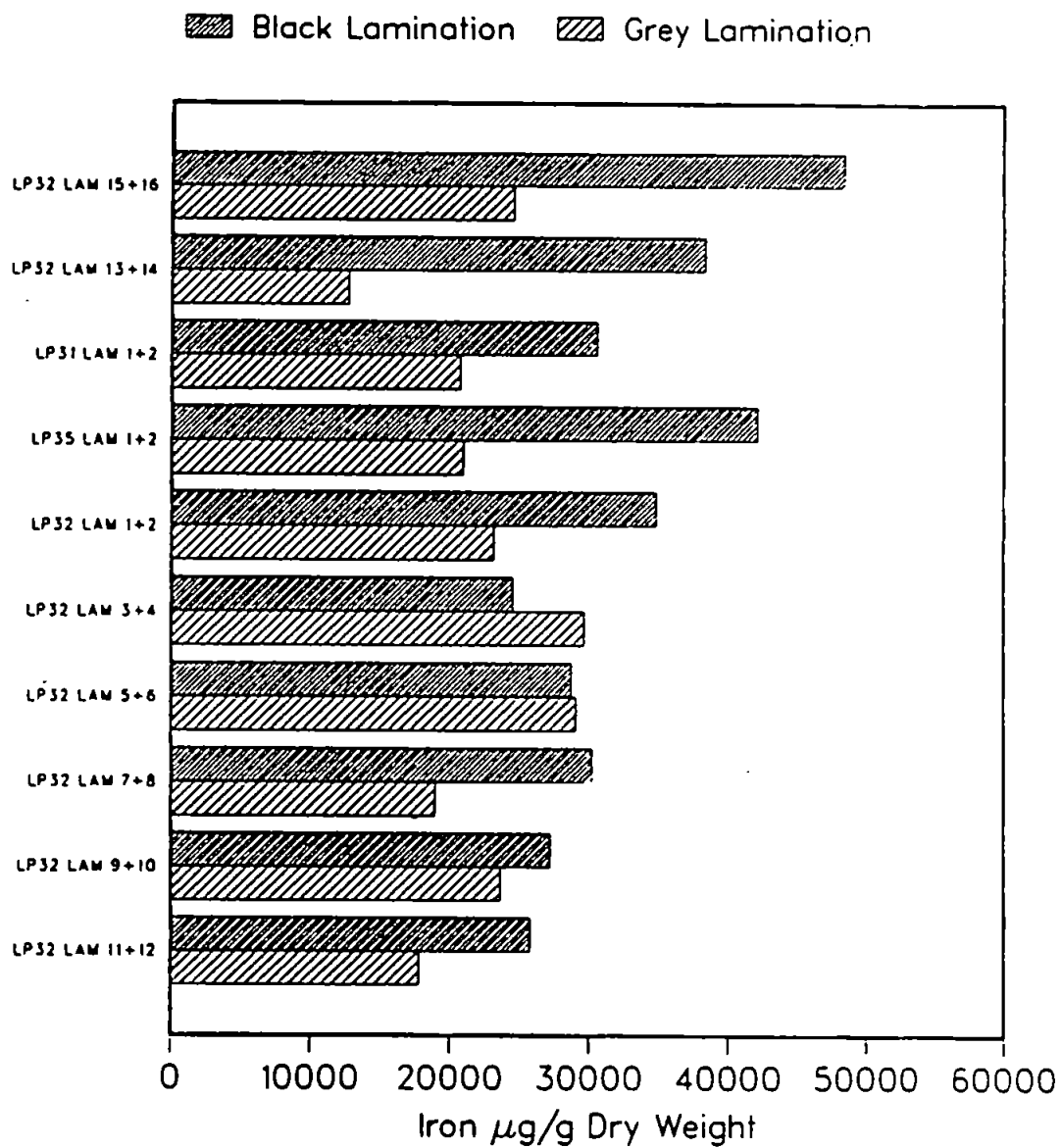
Figure 55. Concentration of Iron in annual laminations of Cores L.P.31,32 and 35 from Loe Pool.

sediment (Fig. 55). This trend is significant ± 1 C. of V. for seven couplets and ± 2 C. of V. for five couplets.

5.5.2 Manganese ′

The distribution of manganese (Mn) in sediment analysed is presented (Fig. 56). The C. of V. for each sample is 4.3%. Like iron the concentration of manganese in Loe Pool sediment is lower than the crustal average and the range is less than other typical lake sediments (Table 15).

In eight of the ten couplets there is a greater concentration of manganese in the grey ⁻ lamination than the corresponding black sediment. This is the inverse of the pattern for iron. This relationship holds for six couplets ± 1 C. of V. and for four couplets ± 2 C. of V.

5.5.3 Iron:Manganese Ratio

The iron:manganese ratio (Fe:Mn) is illustrated in Figure 57. The range is from 46-168. This range is high in comparison with published results from other lake sediments (Table 16). From this Table and by comparison of Figures 57 and 18 it can be seen that the Fe:Mn ratio in the sediment at Loe Pool and Esthwaite Water have a close correspondence.

There is bias in the Fe:Mn ratio between the black and grey laminations. Nine of the couplets have a greater Fe:Mn ratio in the black than grey lamination.

Manganese in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
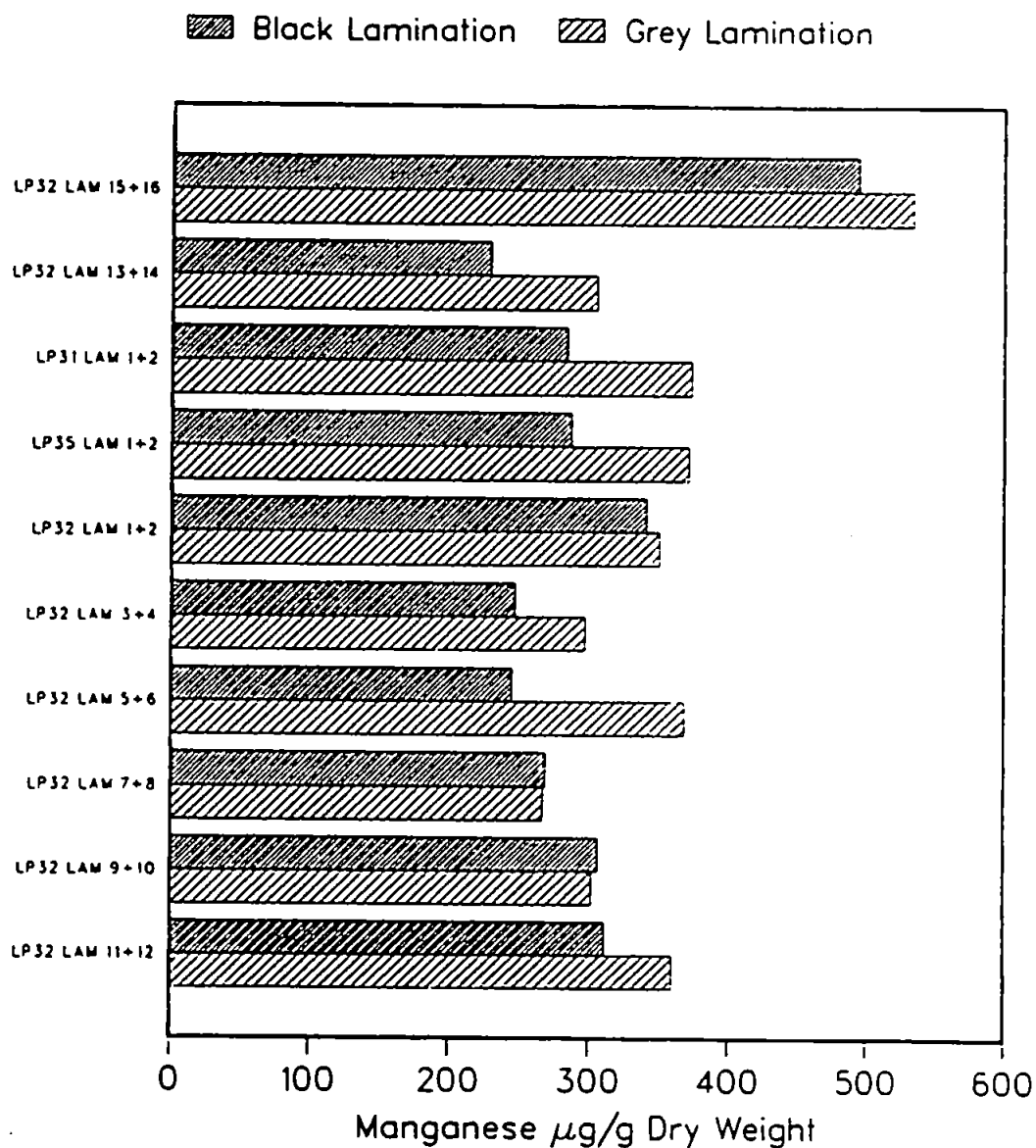
Figure 56. Concentration of Manganese in annual laminations of Cores L.P.31, 32 and 35 from Loe Pool.
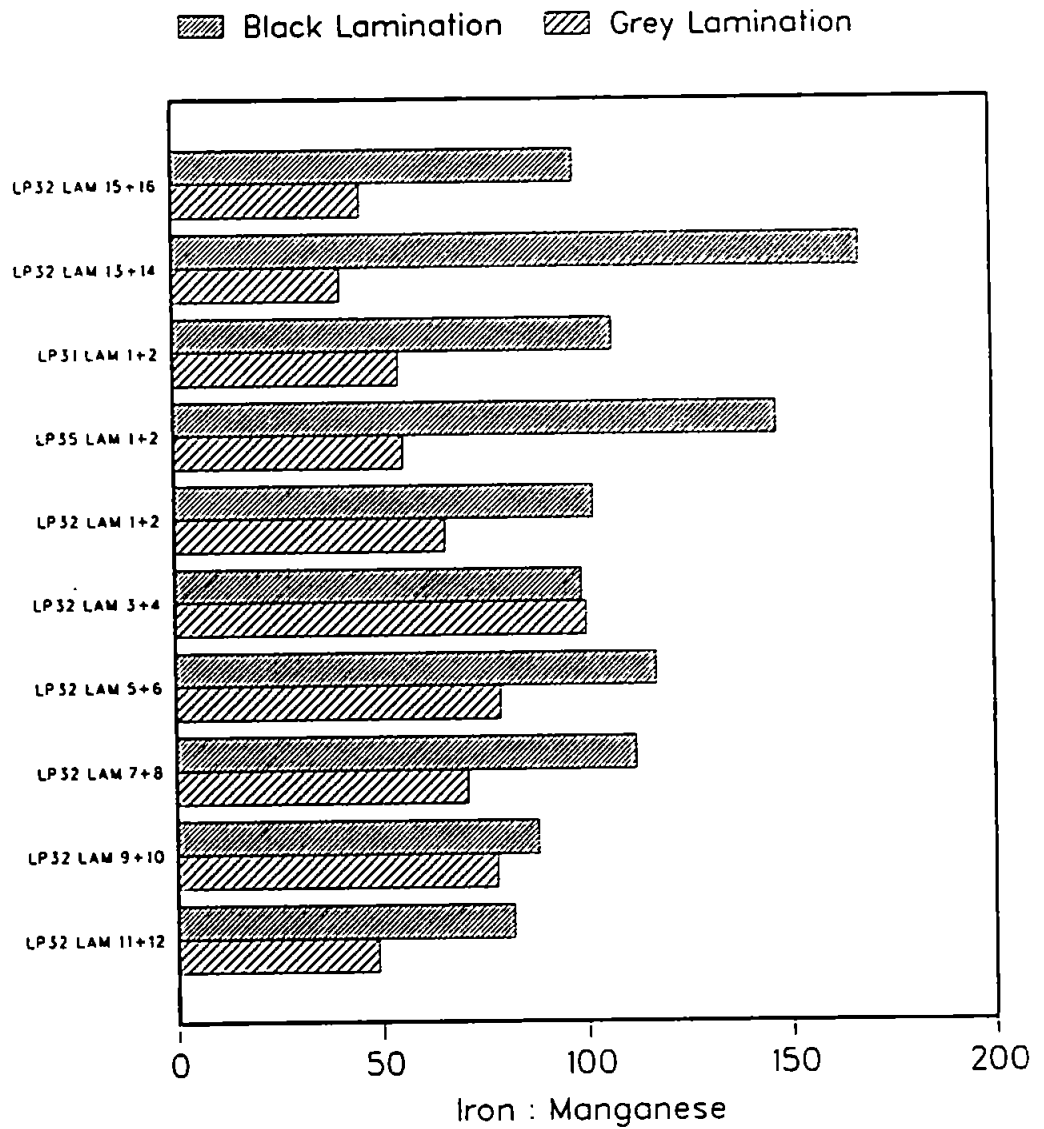
Figure 57. Ratio of Iron : Manganese in annual laminations of Cores L.P.31,32 and 35 from Loe Pool.

Lake	Approximate Fe:Mn Ratio		Reference
	Low	High	
Loe Pool	46	167	This study
Harveys Lake	1	12	Engstrom et al., 1985
Lake of the Clouds	5	30	Anthony, 1977
Windermere South Basin	5	20	)
Ennerdale	25	40	) Mackereth, 1966
Esthwaite	30	120	)

Table 16. Comparison of Fe:Mn Ratio between Loe Pool and other lacustrine sediments.

5.5.4 Sodium, Potassium, Calcium and Magnesium.

The concentration of the elements sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) in the black/grey laminations are shown together with the Ca:Mg ratio (Figs. 58-62). The concentration of each of these elements analysed from Loe Pool sediment are within the ranges quoted for other sites (Table 15). It should be emphasised that the Loe Pool figures are only based on a partial extract. The C. of V. for each element analysed is as follows:

Element	Coefficient of variation %
Na	4.3
Ca	11.4
K	6.7
Mg	19

There are some variations of elemental concentration between the black and grey laminations. For sodium, nine of the varves have a higher concentration in the black (summer) lamination. Statistical treatment shows this relationship is consistent $\pm$ 1 C. of V. in eight of the varves and $\pm$ 2 C. of V. in seven of the varves. There are no such trends in the distribution of potassium and magnesium between the laminations. With potassium six of the varves have a higher concentration in the black (summer) layers and four in the grey (winter) layers. None of the laminations exhibit differences $\pm$ 2 C. of V. The concentrations of magnesium quoted must be treated with caution because of the high C. of V. There is no apparent seasonal trend in the concentration of magnesium
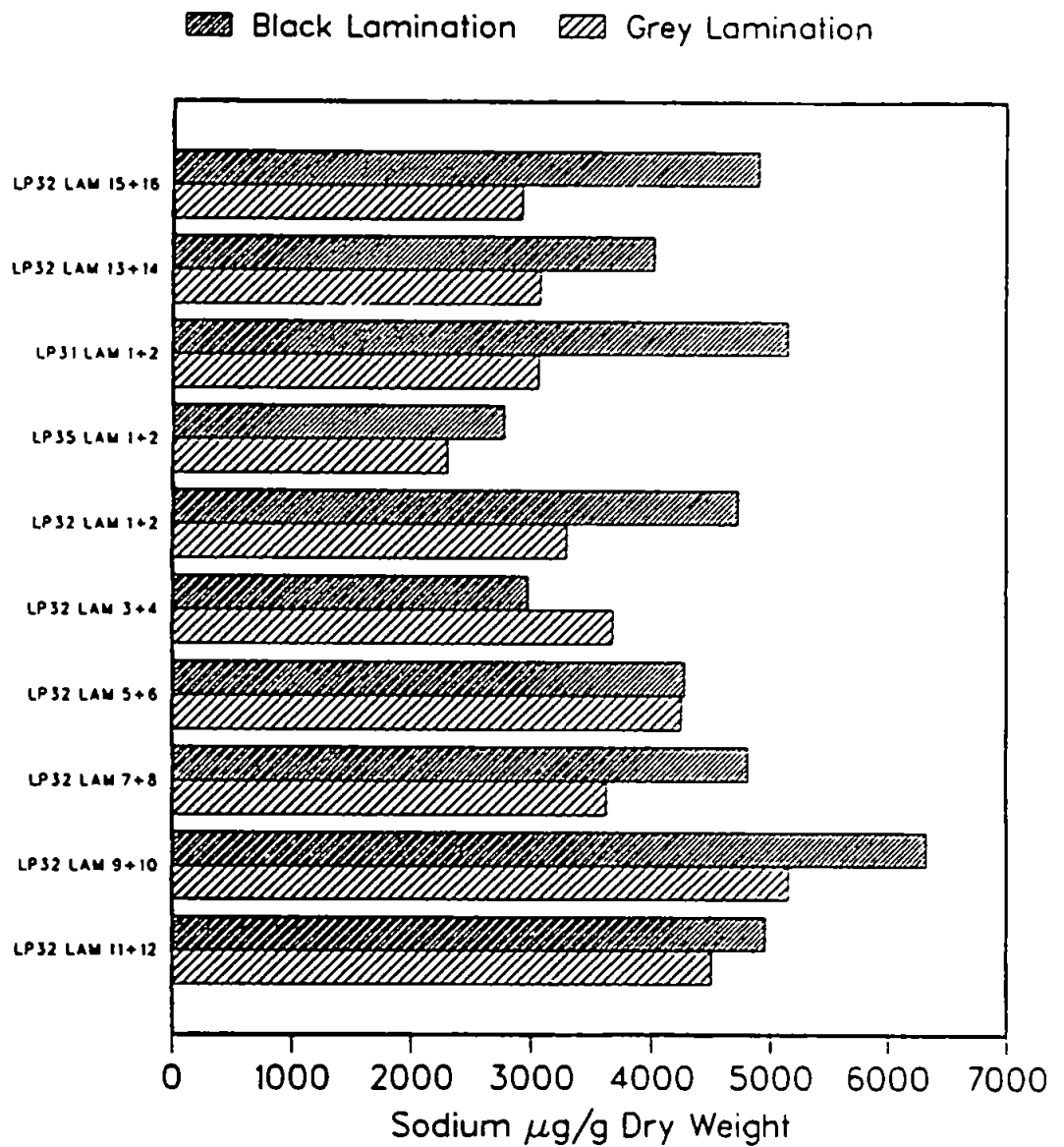
Figure 58. Concentration of Sodium in annual laminations of Cores L.P.31,32 and 35 from Loe Pool.

Potassium in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
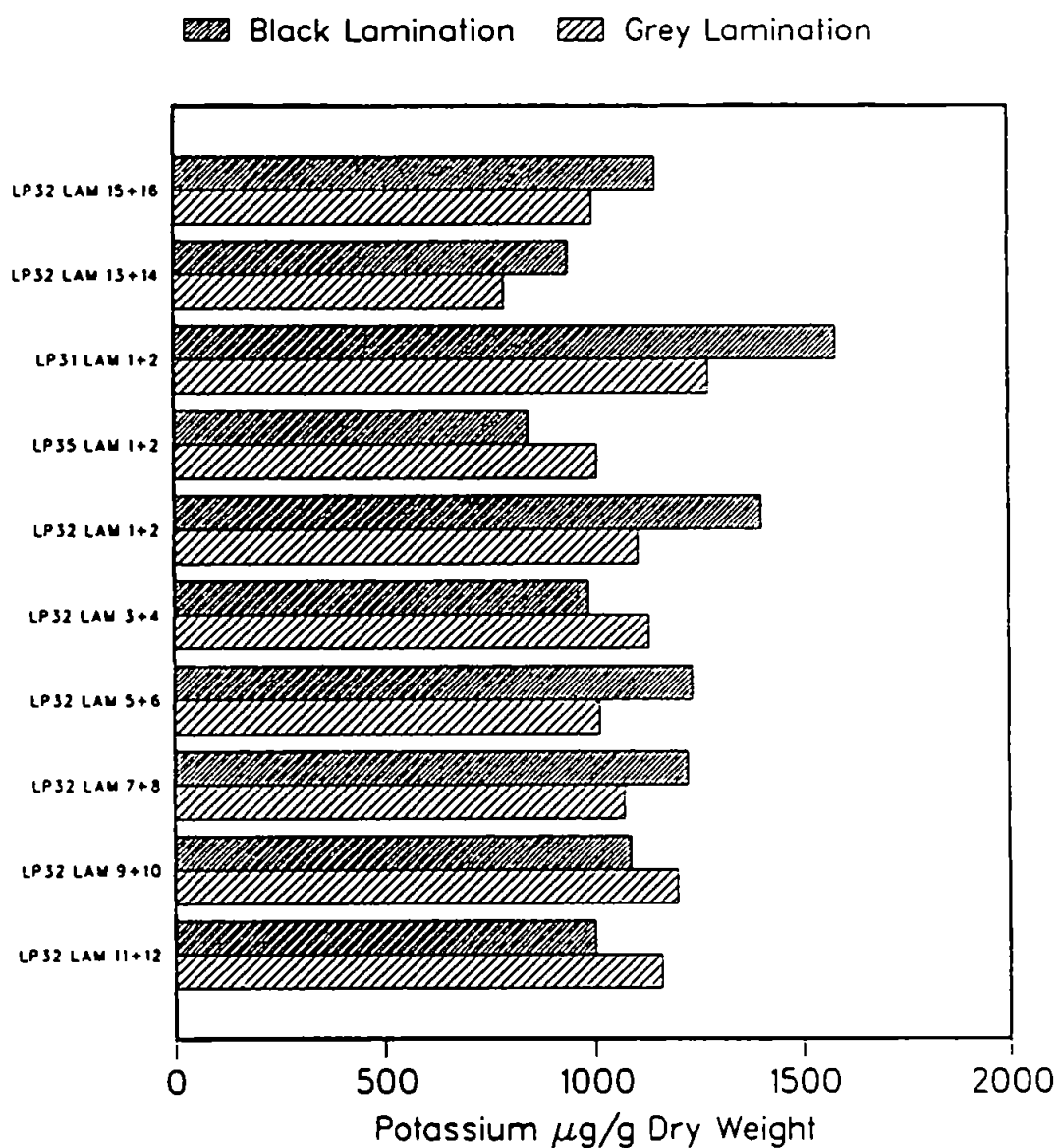
Figure 59. Concentration of Potassium in annual laminations
of Cores L.P.31,32 and 35 from Loe Pool.

Calcium in Loe Pool Sediment

▨▨ Black Lamination   ▨▨ Grey Lamination
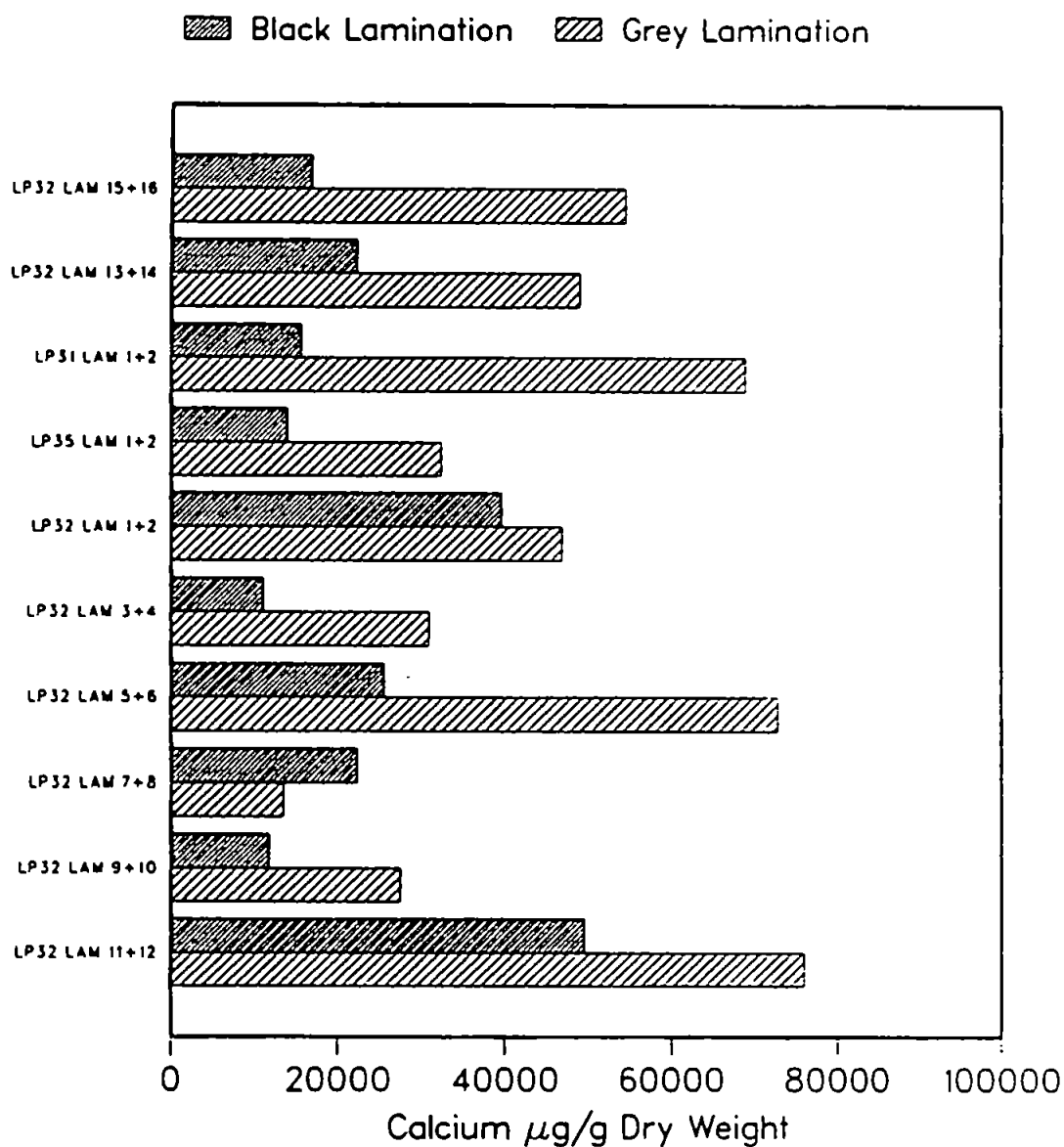
Figure 60. Concentration of Calcium in annual laminations
of Cores L.P.31,32 and 35 from Loe Pool.
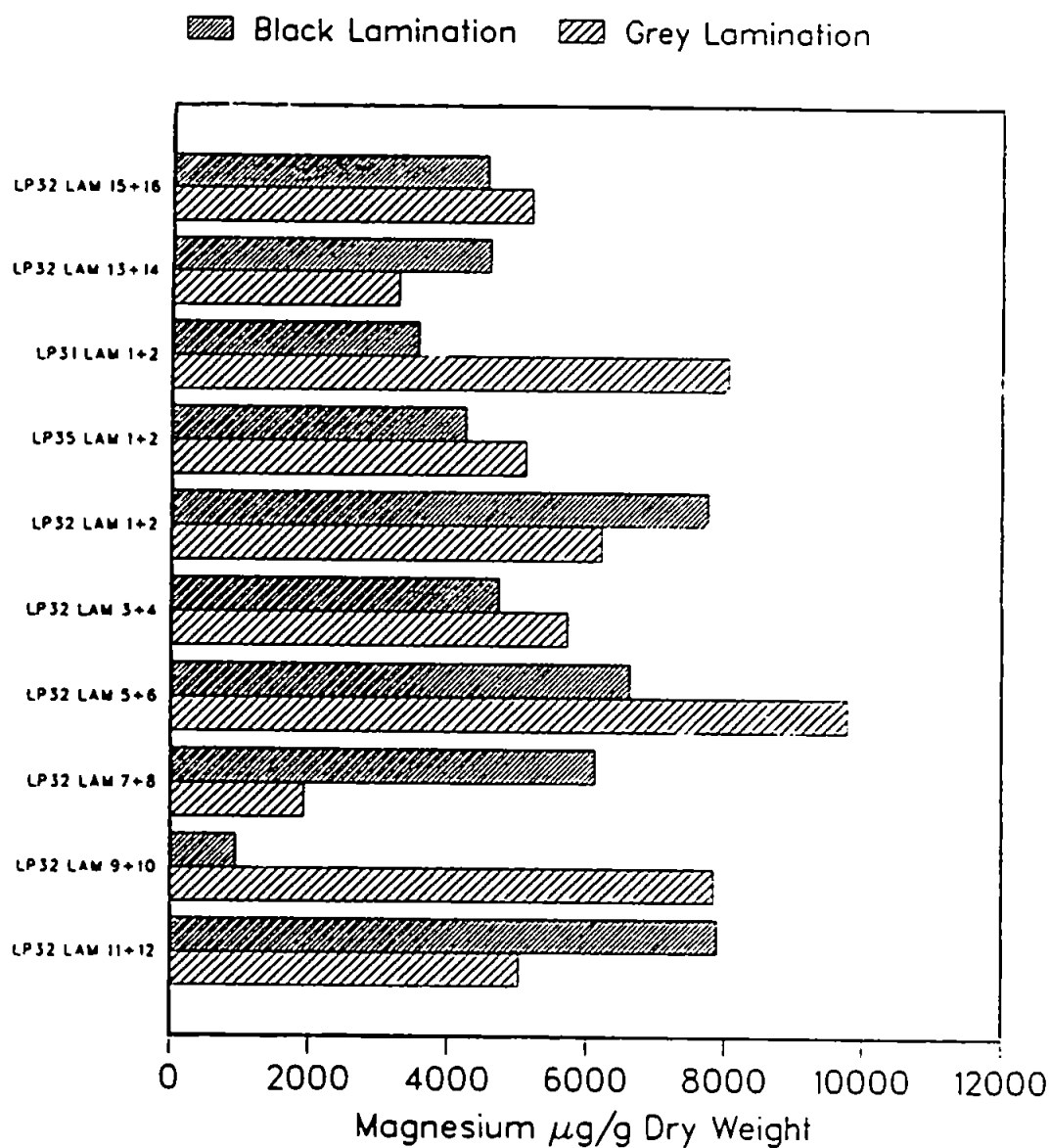
Figure 61. Concentration of Magnesium in annual laminations from Cores L.P.31,32 and 35 from Loe Pool.

Calcium : Magnesium in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
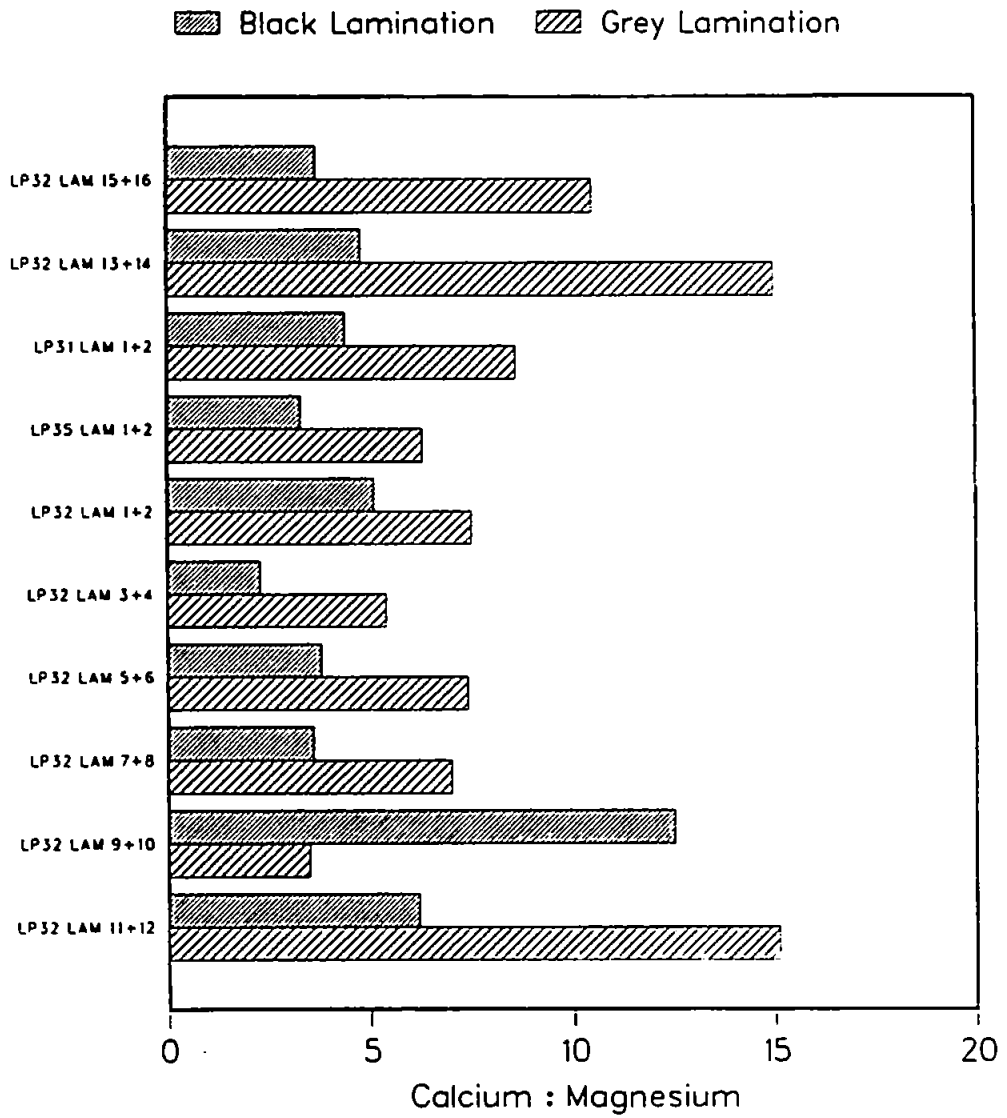
Figure 62. Ratio of Calcium : Magnesium in annual laminations
of Cores L.P.31, 32 and 35 from Loe Pool.

between the black and grey laminations.

In contrast to magnesium the concentration of calcium appears to vary rhythmically. Nine of the grey (winter) laminations have a higher concentration of calcium than the corresponding black (summer) sediment. Of these, eight do so $\pm$ 1 C. of V. and seven $\pm$ 2 C. of V. The ratio of calcium to magnesium is shown in Figure 62. Nine of the ten couplets have a higher ratio in the grey (winter) than the black (summer) sediment. The inconsistent varve (L.P.32 laminations 9+10) may be caused by the particularly low (and possibly spurious) value of magnesium in lamination 9 (Fig. 61).

5.5.5 Lead, Copper, Zinc, Nickel and Cobalt

The concentrations of the heavy metals lead (Pb), copper (Cu), zinc (Zn), nickel (Ni) and cobalt (Co) analysed in Loe Pool sediment are shown in Figures 63-67. The range of the concentration of lead is approximately 160-330 μg/g dry weight (Fig. 63). The analysis had a C. of V. of 2.1%. There are no visual differences in the concentration of lead between the black and grey laminated sediments. The concentration of lead in Loe Pool sediment analysed is in a similar range to other lacustrine sites (Table 15).

The concentration of copper has a range of approximately 500-2000 μg/g dry weight (Fig. 64), and the C. of V. is 2%. There is a higher copper concentration in seven of the black (summer) than grey (winter) laminations. This relationship is significant $\pm$ 2 C. of V. for six varves. There is a considerably higher concentration of copper in Loe Pool sediment than in many other

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Lead in Loe Pool Sediment.
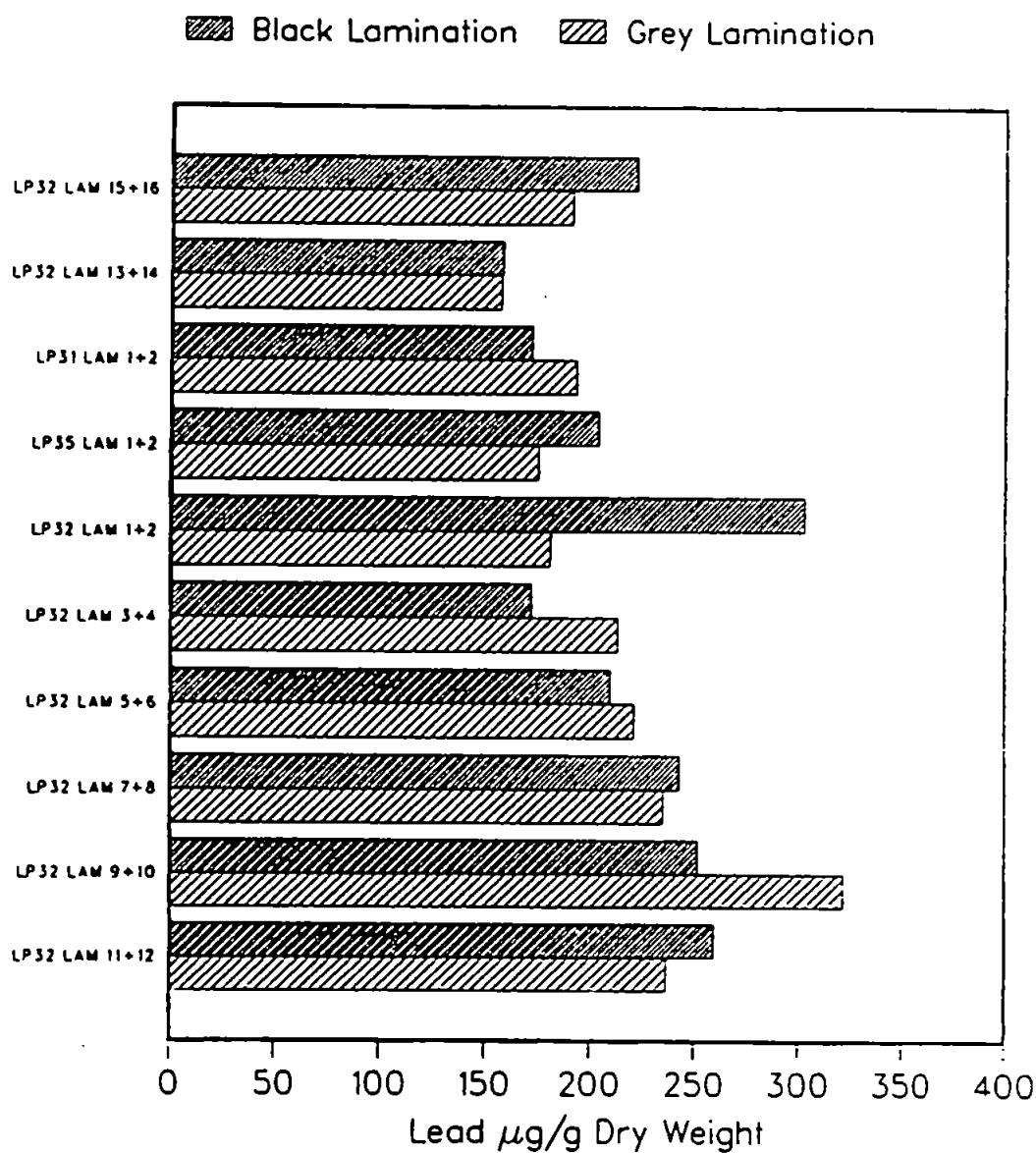
Figure 63. Concentration of Lead in annual laminations of Cores L.P.31,32 and 35 from Loe Pool.

Copper in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
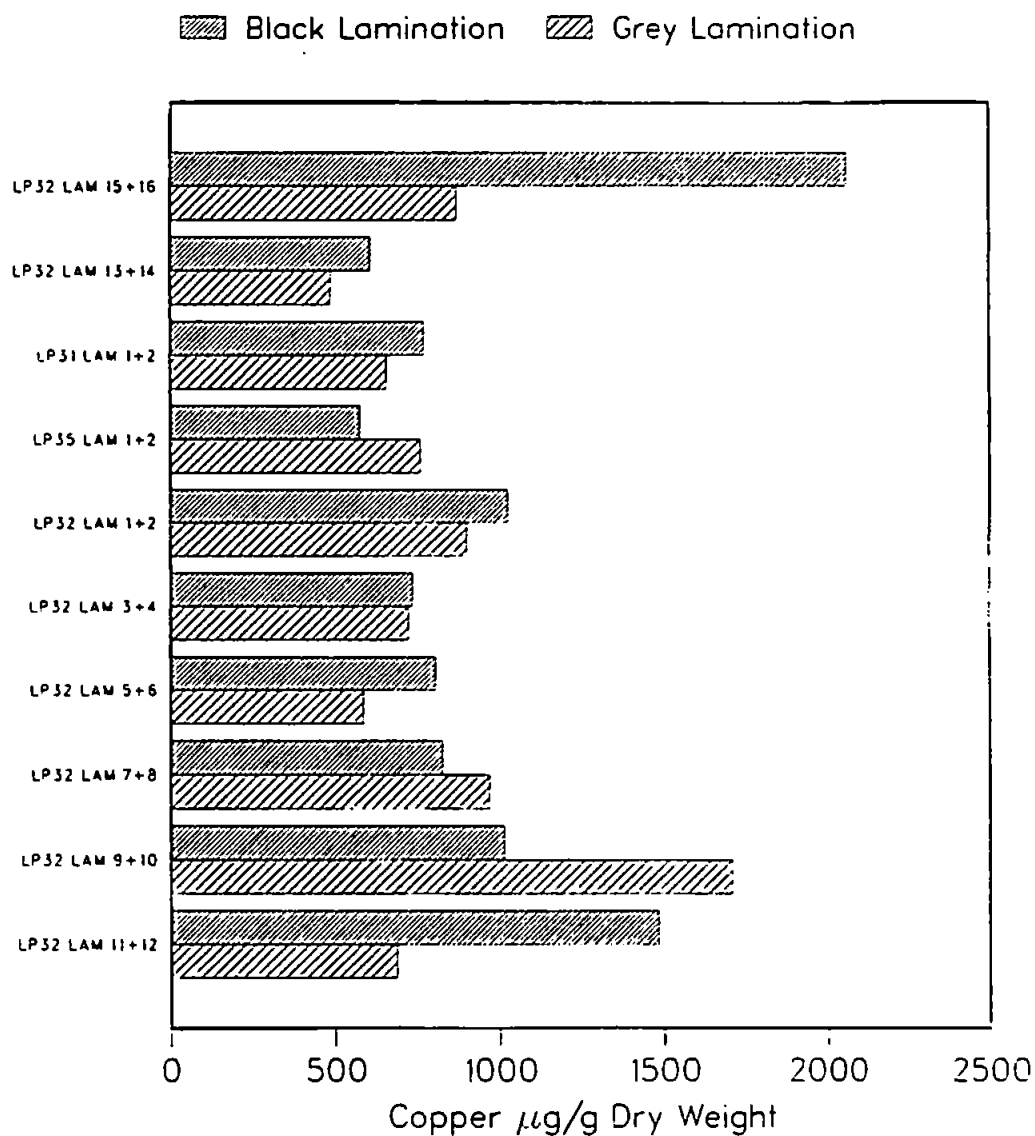
Figure 64. Concentration of Copper in annual laminations
of Cores L.P.31, 32 and 35 from Loe Pool.

Zinc in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
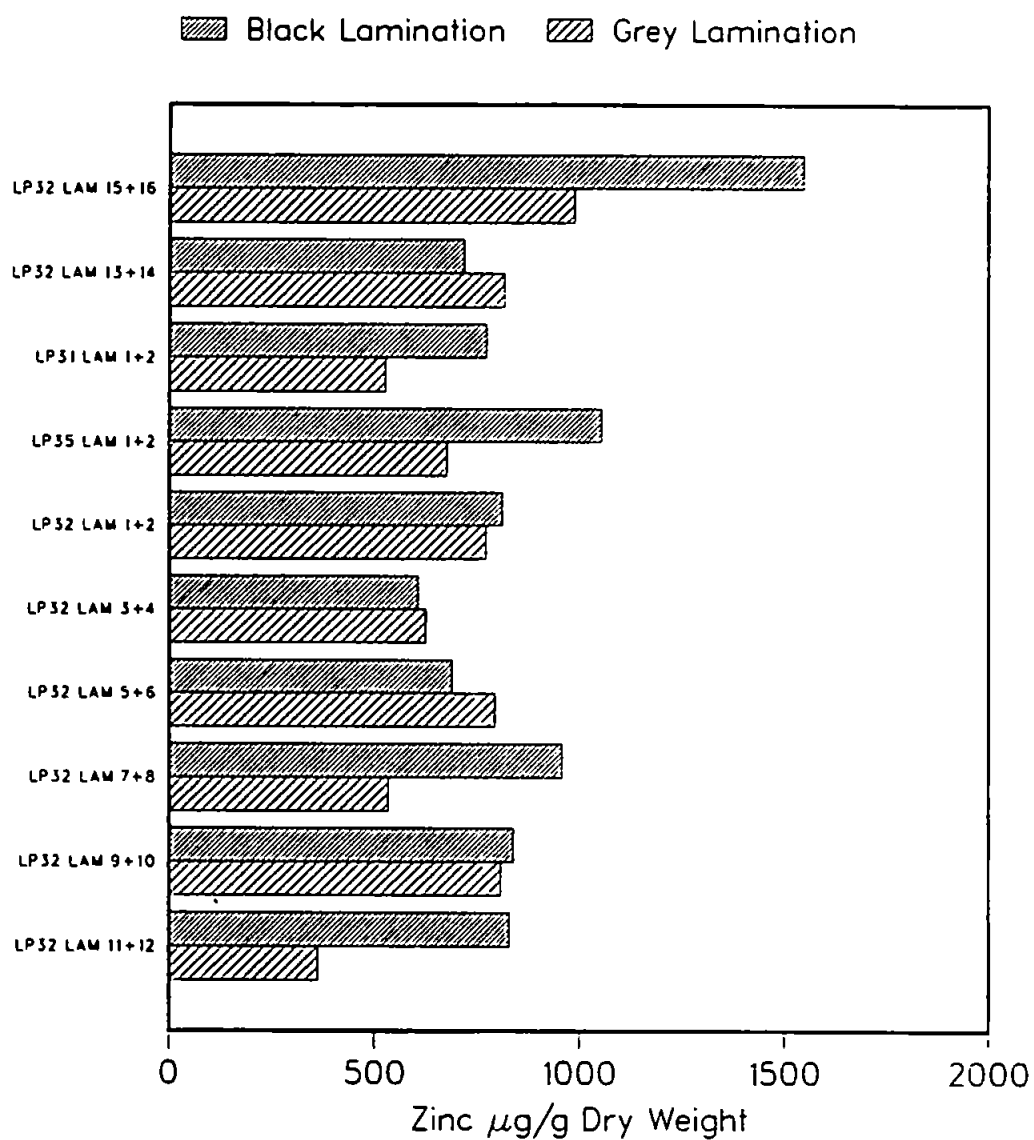
Figure 65. Concentration of Zinc in annual laminations
of Cores L.P.31, 32 and 35 from Loe Pool.
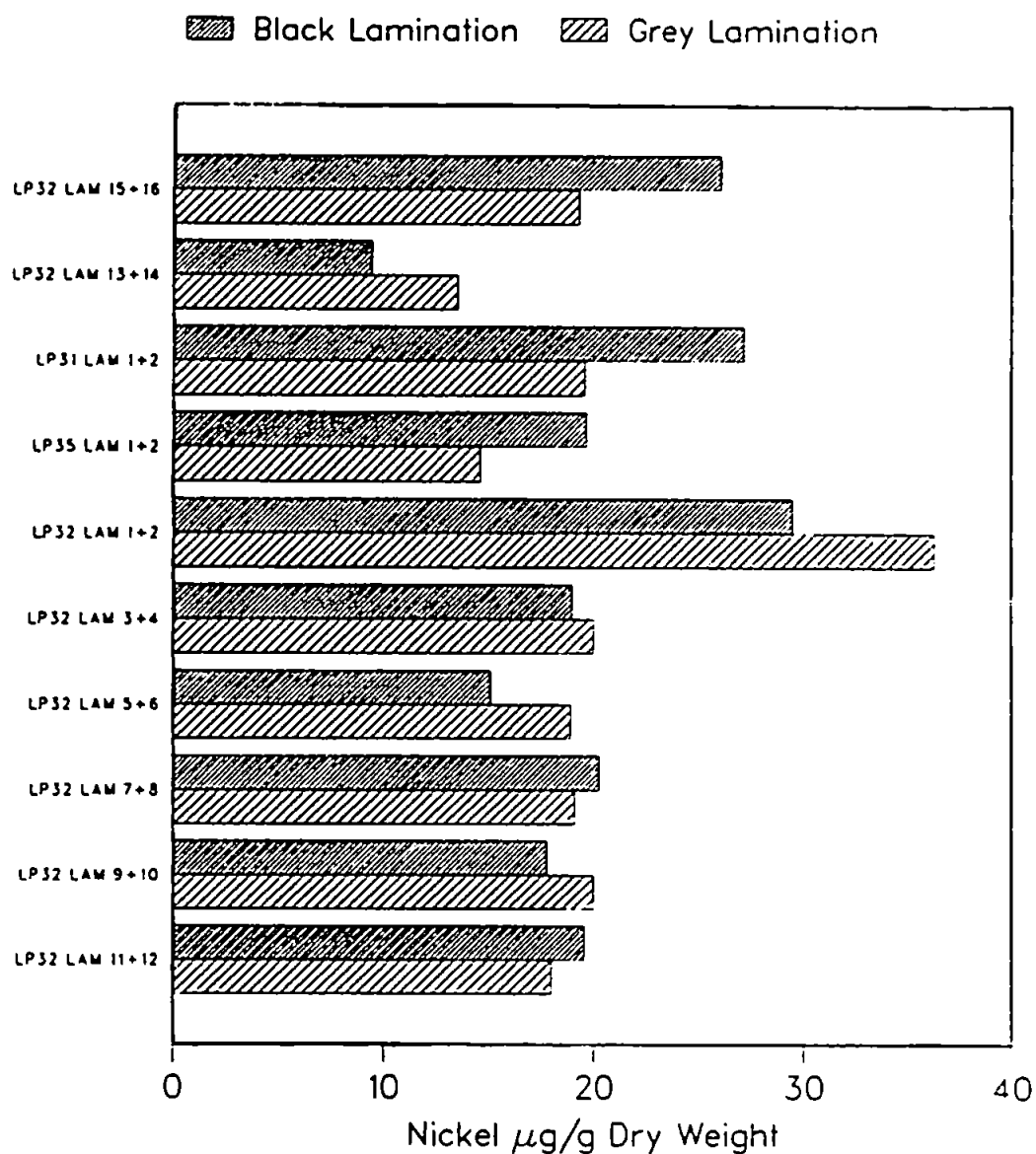
Figure 66. Concentration of Nickel in annual laminations
of Cores L.P.31, 32 and 35 from Loe Pool.

Cobalt in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
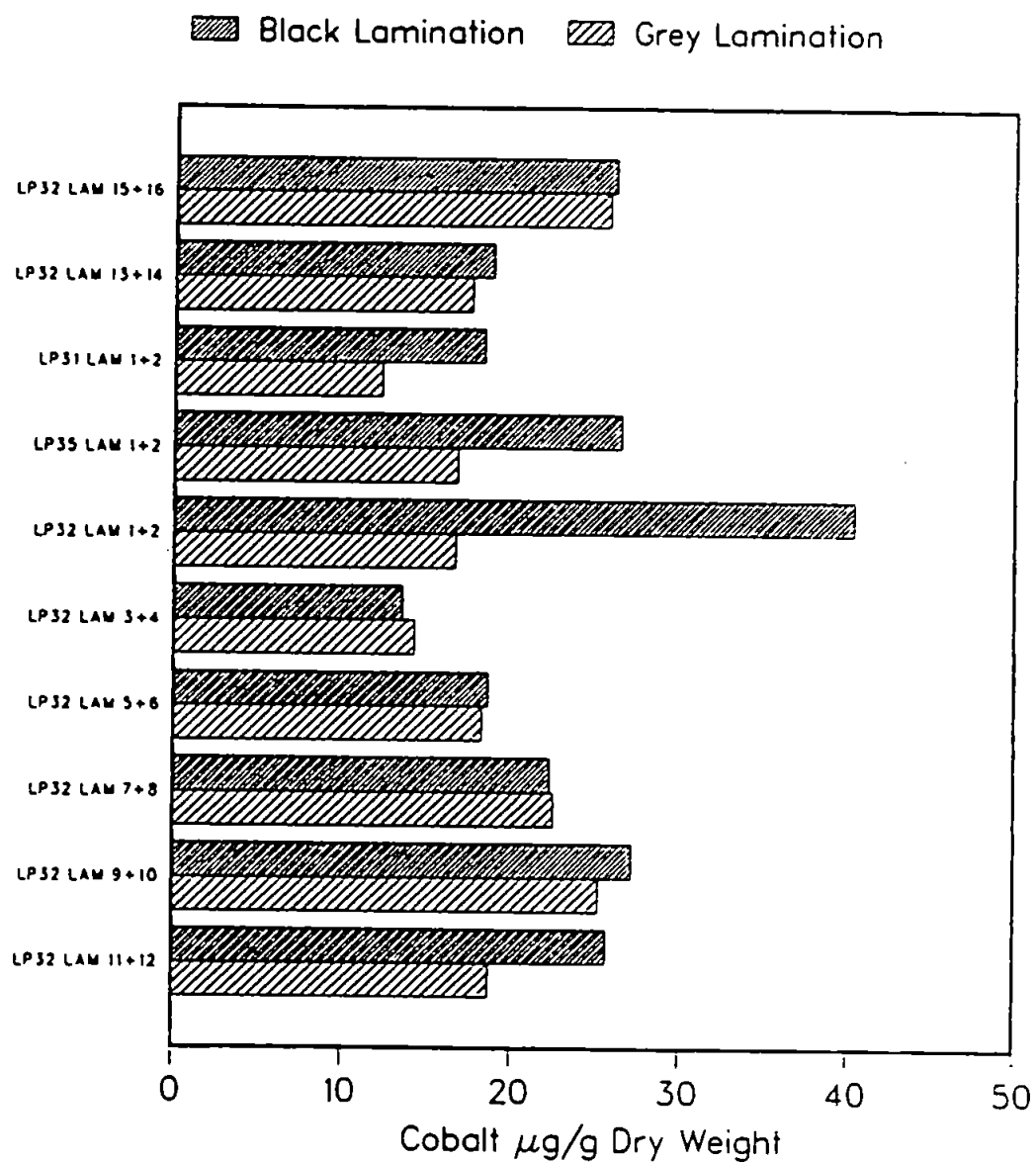
Figure 67. Concentration of Cobalt in annual laminations
of Cores L.P.31, 32 and 35 from Loe Pool.
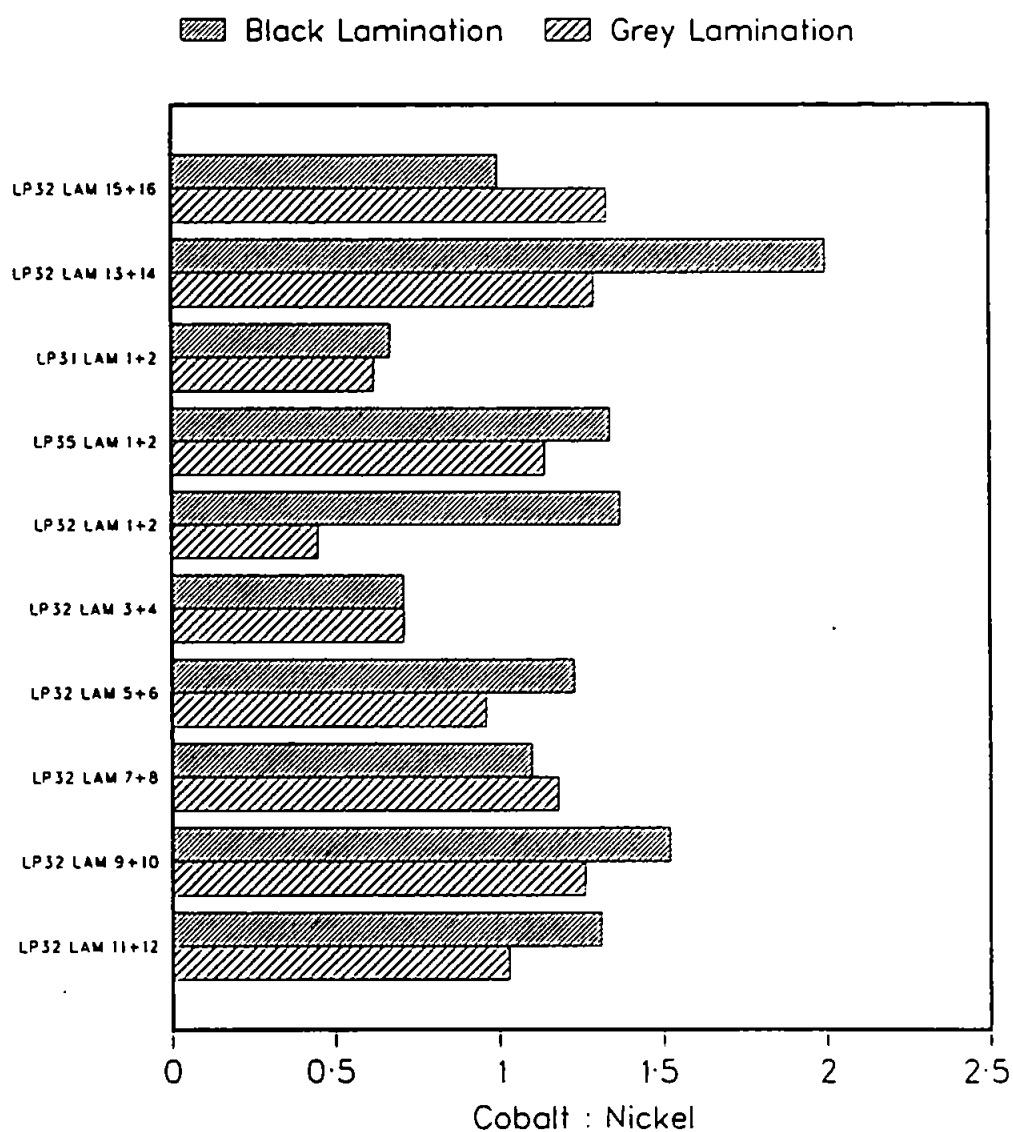
Figure 68. Ratio of Cobalt : Nickel in annual laminations of Cores L.P.31, 32 and 35 from Loe Pool.

lacustrine sediments (Table 15).

Zinc has a range of concentration from 360-1,550 µg/g dry weight (Fig 65). The analytical technique had a relatively high C. of V. of 18%. Seven of the couplets had a higher concentration of zinc in the black than the grey lamination. This variation only holds for five couplets ± 1 C. of V. and one couplet ± 2 C. of V. The range of zinc in Loe Pool sediment is higher than at other sites (Table 15).

The concentration of nickel in the black and grey laminated sediments is illustrated in Figure 66. The element has a range of approximately 10-36 µg/g dry weight. The analysis had a C. of V. of 13%. There is no apparent seasonal bias in concentration and the range is similar to that found in other lake sediments (Table 15).

Cobalt has a range of 12-40 µg/g dry weight in Loe Pool sediment (Fig. 67), with a C. of V. of 14%. Eight of the varves have a higher concentration of cobalt in the black than grey laminations. However, only four varves show this relationship ± 1 C. of V. and 1 varve ± 2 C. of V. The Co:Ni ratio was calculated and is illustrated in Figure 68. Seven of the varves have a greater ratio in the black than grey seasonally-deposited sediment.

5.6 Carbon and Nitrogen

Carbon and nitrogen were quantified in the black and grey laminations using an elemental analyser (section 4.4.5). Results are presented for % organic carbon (Fig. 69), % nitrogen (Fig. 70) and the organic carbon:nitrogen (C:N) ratio (Fig. 71). The

Figure 69. Percentage Organic Carbon in annual laminations of Cores L.P. 31, 32 and 35 from Loe Pool.

% Nitrogen in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
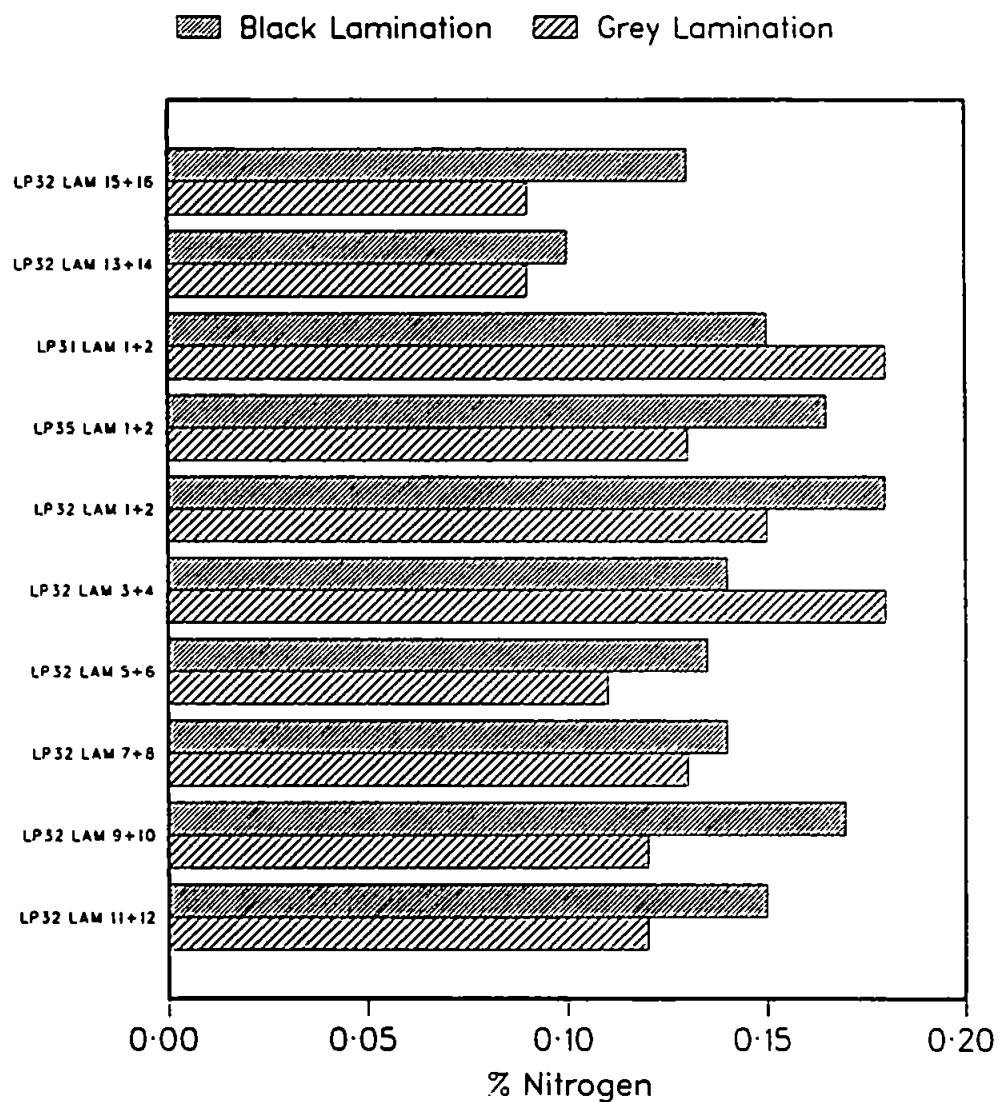
Figure 70. Percentage Nitrogen in annual laminations of Cores L.P.31, 32 and 35 from Loe Pool.
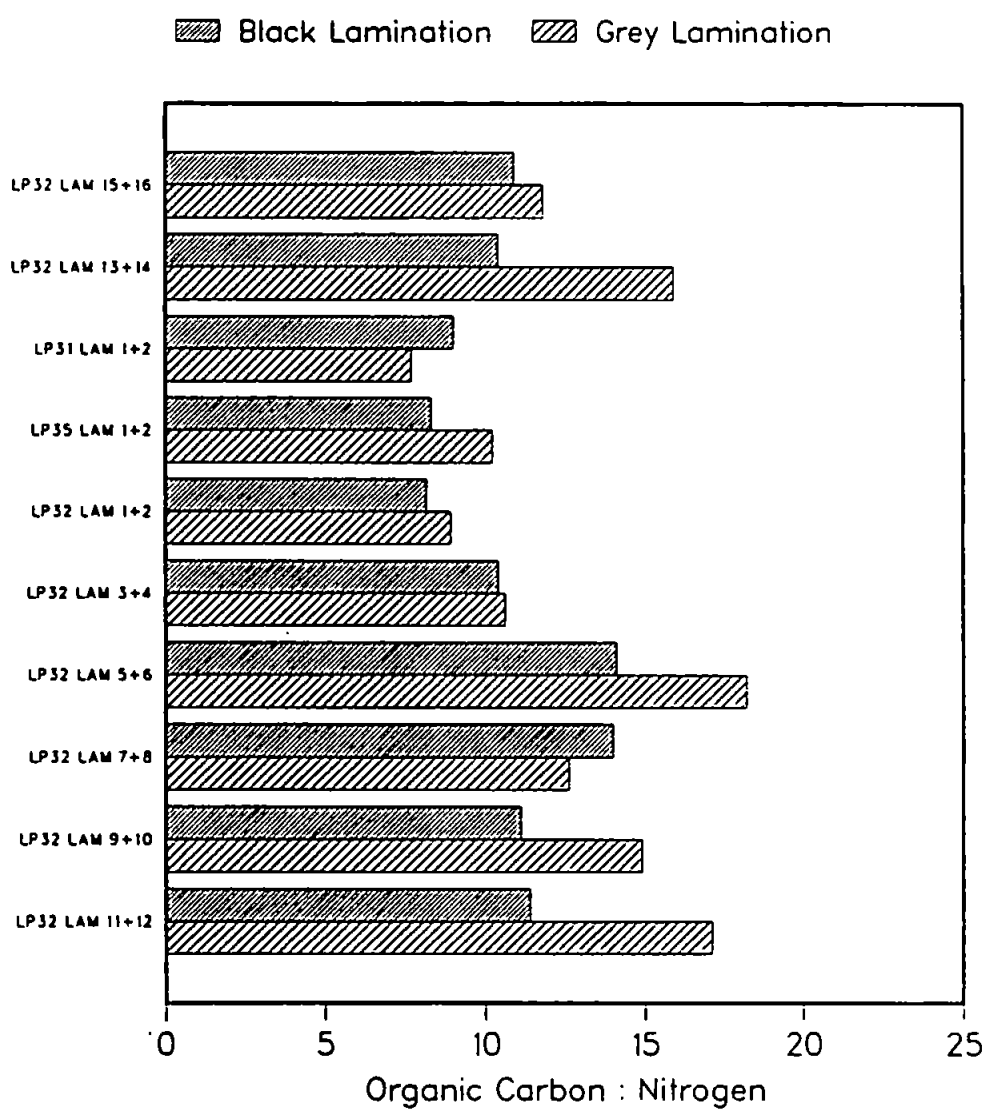
Figure 71. Ratio of Organic Carbon to Nitrogen in annual
laminations of Cores L.P.31, 32 and 35 from Loe
Pool.

coefficient of variation (C. of V.) for the analytical technique based on 2Ø duplicate samples was 11.75% for organic carbon and 14.5 % for nitrogen. The relatively high C. of V. for the techniques probably reflects the low concentration of both organic carbon and nitrogen in the Loe Pool sediment. The concentrations detected were at the lower end of the instrument's analytical range. The range of values of organic carbon, nitrogen and the C:N ratio analysed from Loe Pool, together with values from other lake sediments are shown in Table 17. Organic carbon and nitrogen have a significantly lower concentration in Loe Pool sediment than at other lakes. However, the C:N ratio at Loe Pool is typical of other sites.

There is no apparent seasonality in the concentration of organic carbon. The % nitrogen is higher in the black lamination in eight of the ten varves analysed. However, only two of these summer laminations contain a higher % nitrogen ± 1 C. of V. The C:N ratio also has a seasonal variation. Eight of the grey laminations have a higher ratio than their respective black layers. The average black (summer) C:N ratio is 1Ø.7 compared with 12.8 in the winter.

5.7 Quantification of Humic Acids

The results of the quantification of humic acids (section 4.4.6) present in the black and grey laminated sediments are shown in Table 18.

Only data from two varves are presented because of losses of material during the shaking process. As a consequence any trends

Lake Sediment		Total Carbon (%)	Organic C (%)	Nitrogen (%)	C:N	Reference
Loe Pool		1.5-3	1.2-2.1	0.09-0.18	8-15	This study
English lakes						Summarised by Dean, 1981
Wastewater Thirlmere Buttermere Ennerdale Crummock	least productive	-	6.1	0.49	12	
Haweswater Coniston Rydal Windermere North Basin Derwent Water	intermediate productivity	-	7.1	0.57	13	
Loweswater Windermere South Basin Blelham Tarn Ullswater Bassenthwaite Esthwaite	most productive	-	7.8	0.65	12	

contd.

Table 17. Comparison of % Carbon, % Organic Carbon, % Nitrogen and C:N Ratio from Loe Pool and other Lacustrine Sediments.

Table 17 (contd).		Total Carbon (%)	Organic C (%)	Nitrogen (%)	C:N	Reference
Lake Sediment						
Windermere:	Sept.				6.4	Hamilton-Taylor
	Oct.				6.8	et al., 1984
	Nov.				8.1	
	Dec.				6.9	
	Jan.				10.0	
	Feb.				10.3	
	Mar.				10.9	
	Apr.				7.1	
	May				6.4	
	June				6.1	
	July				5.4	
	Aug.				1.8	

Core	Colour of lamination	Presumed season of deposition	Weight humic acids g/g dry weight
LP 31 lam 1	black	summer	0.0216
LP 31 lam 2	grey	winter	0.017
LP 32 lam 1	black	summer	0.030
LP 32 lam 2	grey	winter	0.0208

(lam = lamination)

Table 18. Quantification of Humic Acids in Loe Pool Sediment.

in the results must not be over-emphasised. However, in the varves
analysed there are approximately 1.3 times more humic acids present
in the black (summer) than grey (winter) laminations.

5.8 Carbonate

The carbonate concentration of the black and grey laminations
analysed from cores L.P.31, L.P.32 and L.P.35 was determined by
elemental analysis (section 4.4.5). The results are presented in
Figure 72. The technique had a C. of V. of $\pm$ 11.9%. The range
of concentration was from 0.24 to 1.64%. This is low in comparison
with other carbonate containing lakes (Table 19).

The laminated sediment from Loe Pool exhibited a marked seasonal
bias in % carbonate (Fig. 72). All ten of the varves analysed had a
higher concentration of carbonate in the grey (winter) than black
(summer) layers. This trend was consistent $\pm$ 1 C. of V. for nine
varves and $\pm$ 2 C. of V. for seven varves.

5.9 Pigment Content of Loe Pool Sediment

Pigments were extracted and analysed from core L.P.6 and from a
series of black and grey annual laminations from cores L.P. 31,
L.P. 32 and L.P. 35. The pigments chlorophyll a, chlorophyll b
and chlorophyll c were quantified in the brown clay gyttja,
black/red laminations and grey clay present in L.P.6. The analyses
were based on the extraction and spectrophotometric detection
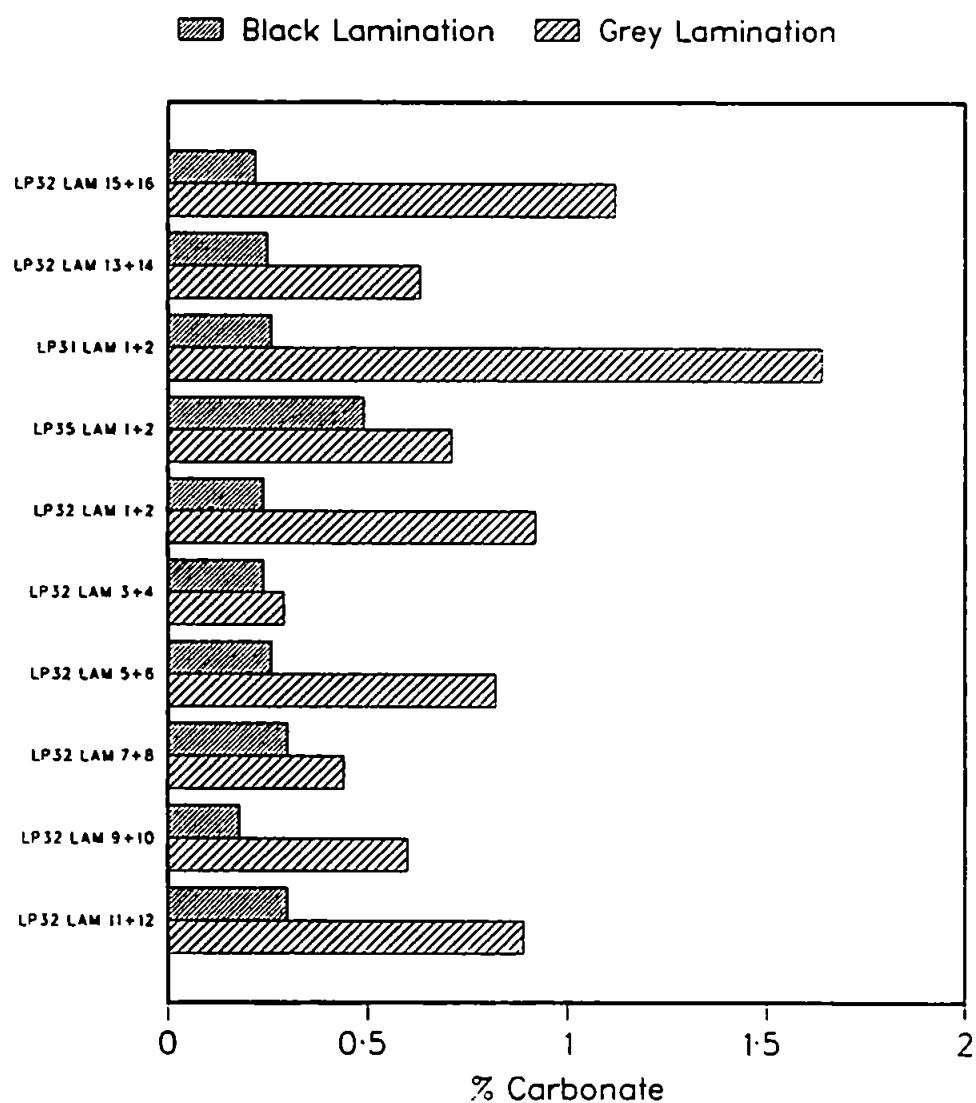
Figure 72. Percentage carbonate in annual laminations of Cores L.P.31, 32 and 35 from Loe Pool.

Lake Sediment	% Carbonate g^{-1} dry weight
Loe Pool (a)	0.24 - 1.64
Ontario (b)	5.0
Erie (b)	5.9
Huron (b)	5.8
Mendota, Wisconsin (b)	35
La Belle, Wisconsin (b)	45
16 English Lakes (b)	0

(Source: (a) This study; (b) Dean, 1981)

Table 19. Comparison of % Carbonate in Loe Pool and other Lacustrine Sediments.

techniques described in section 4.4.7.1. Pigments present in the individual black and grey seasonal laminations sliced from cores L.P.31, L.P.32 and L.P.35 were analysed using the H.P.L.C. separation and fluorescence and absorbance detection method (section 4.4.7.2). All results are presented in horizontal bar chart form and annotated with the lamination's colour (for example Fig. 73). Units are microgrammes pigment per gramme dry weight sediment.

5.9.1 Chlorophylls a, b and c in Core L.P.6

The concentration of chlorophylls a, b and c in the individual laminations and grey clay sliced from core L.P.6 are shown (Figs. 73-75). Each plot shows a similar trend of chlorophyll concentration, increasing from the bottom of the sediment core to the top. The grey clay deposited in the early 1930's has a low and fairly uniform concentration of chlorophyll pigments. During the period of intense mining, when the red haematite clay was deposited the pigment concentration is reduced to a minimum value (Figs. 73-75). Following the cessation of mining and the development of the brown clay gyttja the concentration of each chlorophyll pigment rises. At the sediment surface the pigment concentration decreases, this may not be a real decrease but an error in assessing % dry weight, in this the most liquid sediment. For chlorophylls a, b and c some of the higher pigment concentrations are associated with the darker coloured sediment, and the lower concentrations with lighter coloured sediment.

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Chlorophyll a in Loe Pool Sediment Core LP6
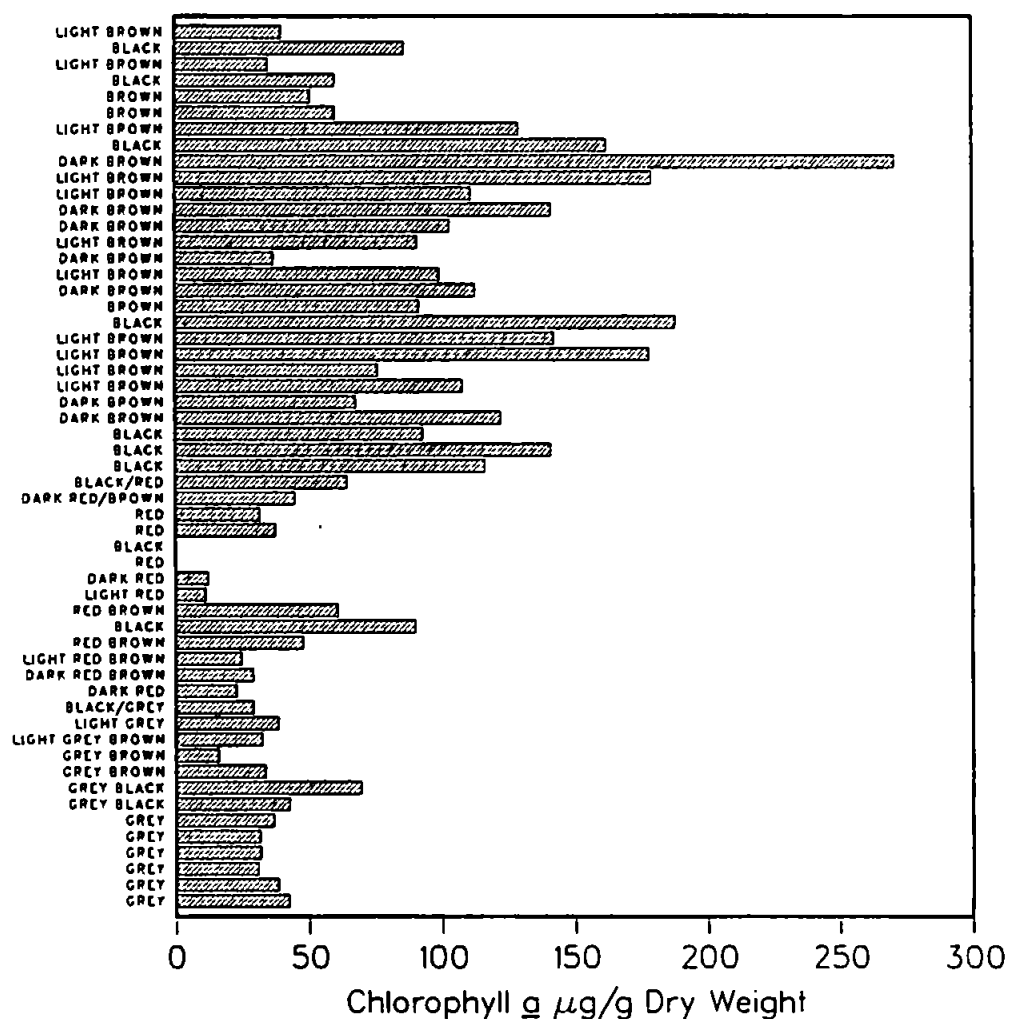
Figure 73. Concentration of Chlorophyll a in Core L.P.6 from Loe Pool.

Chlorophyll b in Loe Pool Sediment Core LP6
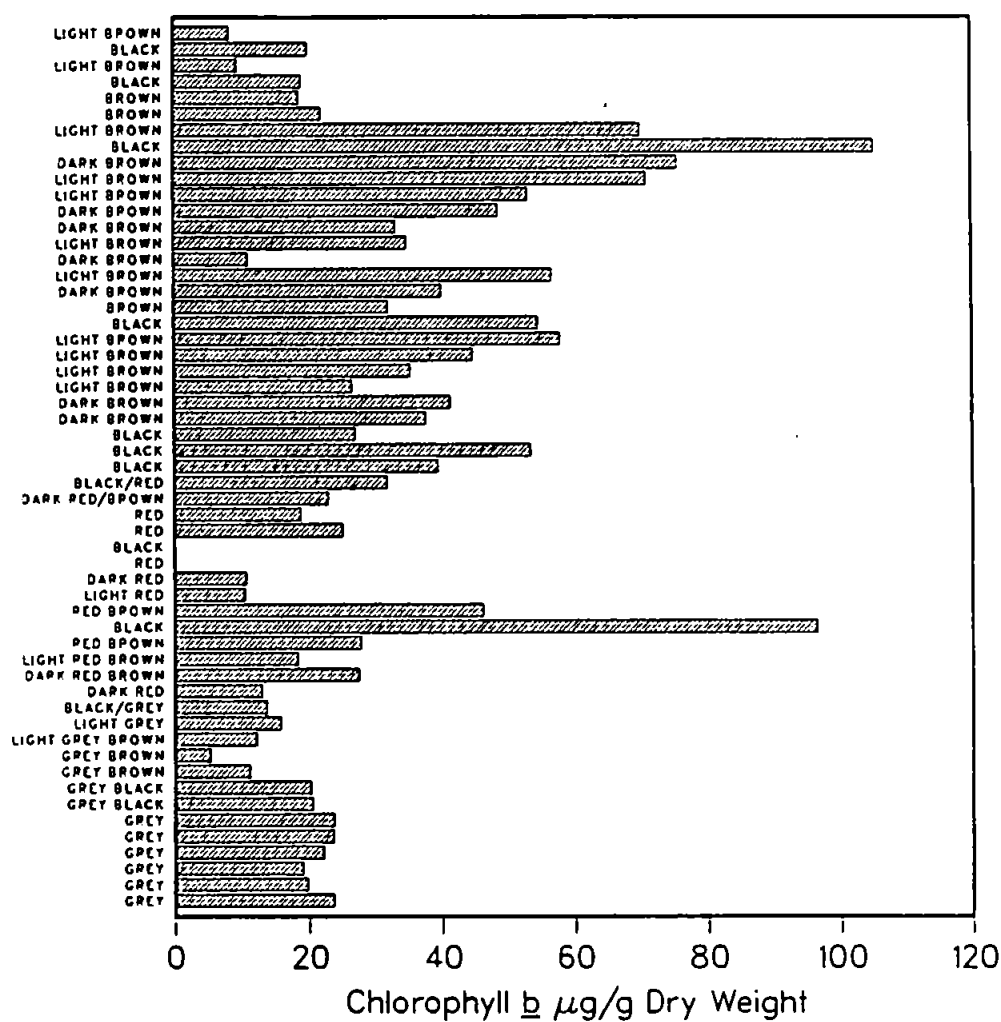
Figure 74. Concentration of Chlorophyll b in
Core L.P.6 from Loe Pool.

Chlorophyll c in Loe Pool Sediment Core LP6
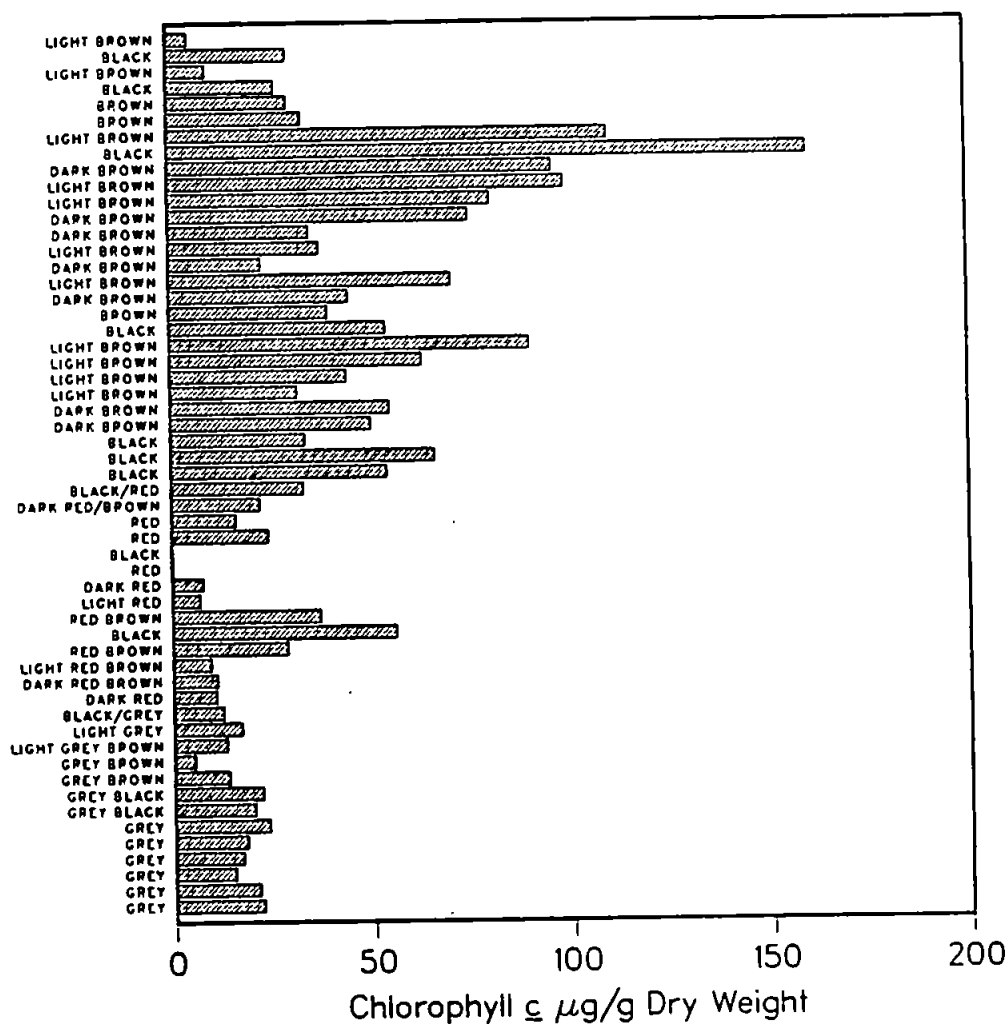
Figure 75. Concentration of Chlorophyll c in Core L.P.6 from Loe Pool.

The range of concentration for each pigment is shown in Table 20. Each pigment exhibits little change of concentration in the grey clay. In the black/pink laminated clay the highest concentration of pigment occurs in the black lamination and the greatest range of values with chlorophyll b.

The averages of chlorophylls a, b and c analysed in each stratigraphic unit of L.P.6 are shown in Table 21. It is apparent from Tables 20 and 21 that there is a greater concentration of chlorophyll b than c in the black/pink and grey clays, yet more chlorophyll c than b in the brown clay gyttja.

5.9.2 Correlation Coefficients between Chlorophyll a and other Variables Measured from Core L.P.6

Correlation coefficients were calculated between chlorophyll a, loss on ignition and dry weight. These are shown in Table 22. There are negative correlations between the concentration of chlorophyll a and the dry weight of the whole core and the red/pink and grey laminated sediment. In contrast, for the same sections of core there are positive correlations between chlorophyll a and loss on ignition values.

5.9.3 Chlorophylls, their · Degradation Products and Carotenoids in the Black and Grey Laminated Sediment.

Pigments extracted from individual laminations were separated by H.P.L.C. and detected by absorbance and fluorescence detectors (section 4.4.7.2). A typical chromatogram is illustrated (Fig. 76).

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Sedimentary Unit	Chl a	Chl b	Chl c
Brown clay gyttja	40*-270	10*-105	30*-170
Pink/black laminations	10-90	10-100	10-60
Grey clay	30-40	20-23	20-23

*ignoring low concentration at sediment surface

Table 20. Range of Pigment Concentrations in g/g dry weight from Core L.P.6.

Sedimentary Unit	Average Concentration of Chlorophylls		
	a	b	c
Brown clay gyttja	110.4	40.96	55.3
Pink/red laminations	38.8	23.5	19.2
Grey clay	35.1	22.0	19.4

Table 21. Average Concentration of Chlorophylls a, b and c in g/g dry weight from Core L.P.6.

Whole or section of Core L.P.6	First Variable	Second Variable	Correlation Coefficient	t
Whole core	Chl a	D.W.	- 0.60	7.05***
Brown clay gyttja	Chl a	D.W.	+ 0.10	1.65*
Pink/black & grey clay	Chl a	D.W.	- 0.56	4.33***
Whole core	Chl a	L.O.I.	+ 0.71	12.36***
Brown clay gyttja	Chl a	L.O.I.	+ 0.38	3.52**
Pink/black & grey clay	Chl a	L.O.I.	+ 0.69	5.5***

Chl a   = Chlorophyll a
D.W.   = Dry weight
L.O.I. = Loss on ignition

Table 22. Correlation Coefficients between selected variables from Core L.P.6.

*not significant

** significant 0.005 < p < 0.001

*** significant 0.001 < p < 0.0005
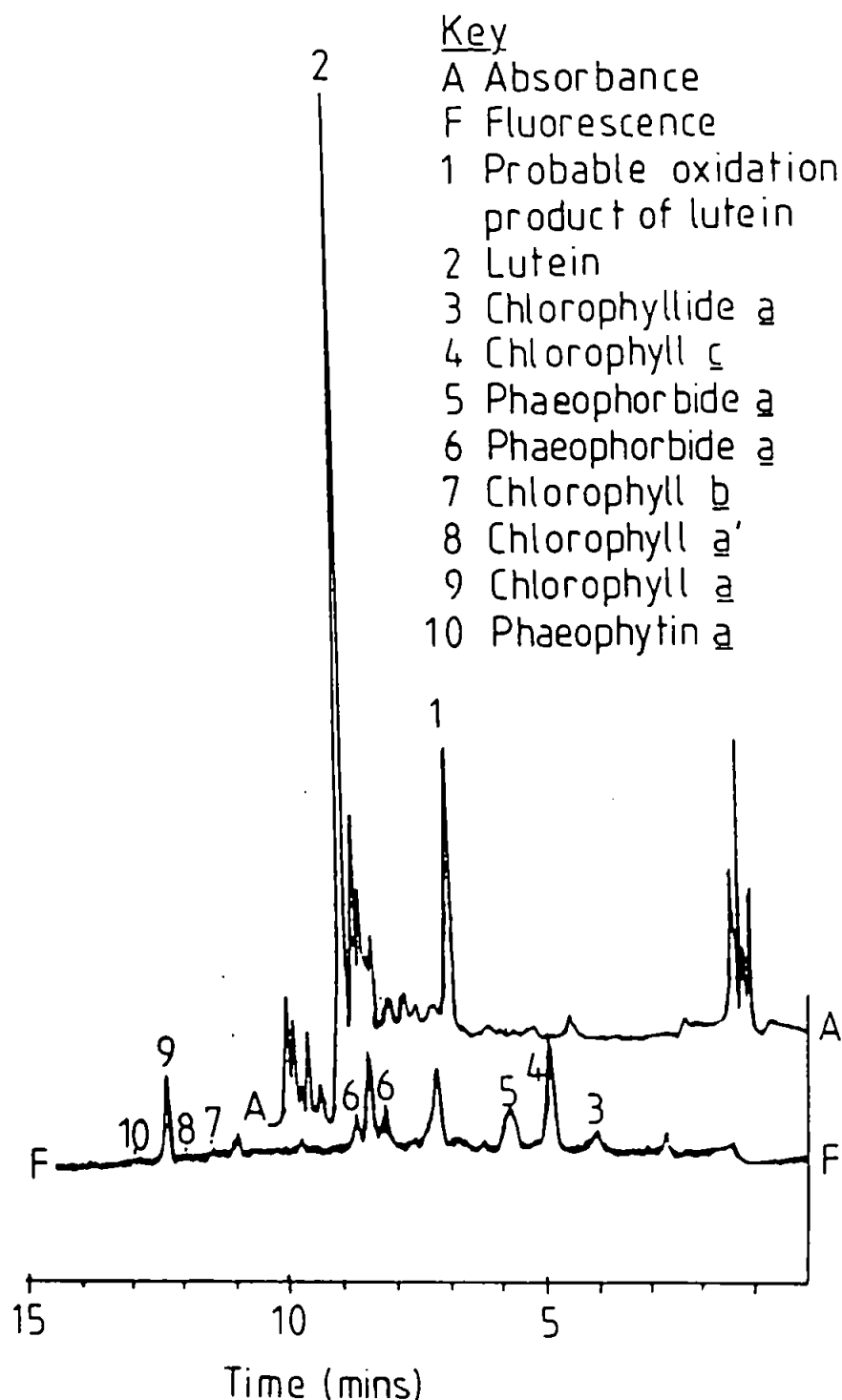
Figure 76. High Pressure Liquid Chromatography Absorbance (A) and Fluorescence (F) chromatograms of a sediment extract from Loe Pool. Details of operation in section 4.4.7.2.

Both carotenoids and chlorophylls are detected by absorbance, additionally the chlorophylls are detected by their fluorescence. Carotenoids were identified by absorbance spectrum and retention time data, the chlorophylls by retention time data only. Identities of peaks are noted on Figure 76. The concentration of the major chlorophylls and phaeopigments were calculated according to the method described in section 4.4.7.2. These results are presented in Figures 77-81.

Chlorophyll a was included with the allomer product chlorophyll a', the range present was from 0.05-3 µg/g dry weight. Because there is a significantly higher concentration in L.P.31 laminations 1 and 2, and L.P.35 lamination 1 two of the plots are also presented with a logarithmic x axis.

The concentration of chlorophyll c in the seasonally deposited black and grey laminations is shown (Fig. 79). The range is from 0.015-0.08 µg/g dry weight. All of the nine varves examined had a higher concentration of chlorophyll c in the black (summer) than grey (winter) layers.

The profile of the concentration of chlorophyll degradation products termed the "phaeopigments" are illustrated with normal and logarithmic scales (Figs. 80 & 81). In this study the term phaeopigments included phaeophytins, phaeophorbides and the chlorophyllides. The range is from 0.1-6.5 µg/g dry weight. The profile is similar to that for chlorophyll a and a' with high values in L.P.31 lamination 1+2 and L.P.35 lamination 1. There are higher concentrations of phaeopigments in each of the black than grey laminations. In addition, the ratio of phaeopigments:chlorophyll a + a' was calculated (Fig. 82). The

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Chlorophyll a + a' in Loe Pool Sediment

Black Lamination   Grey Lamination
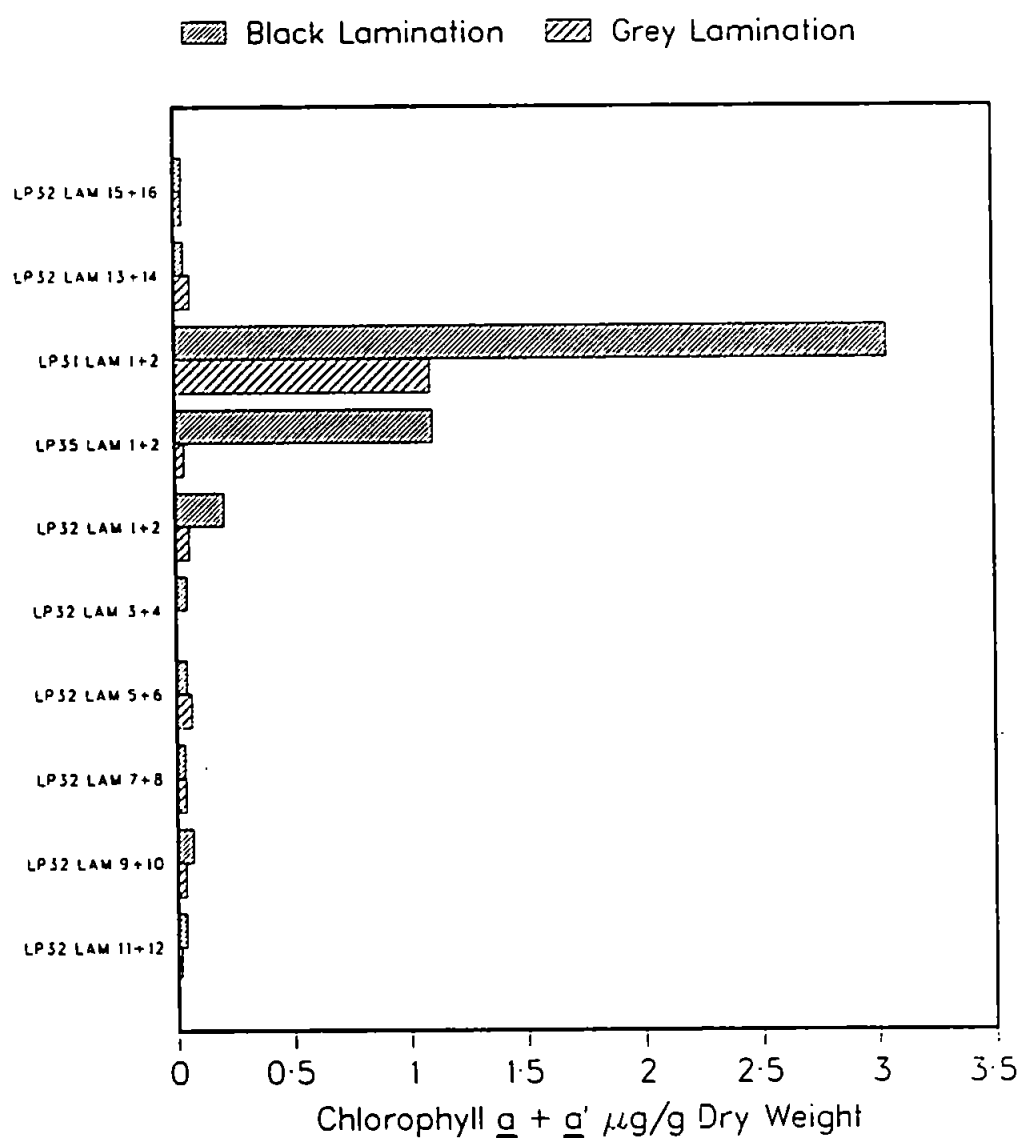
Figure 77. Concentration of Chlorophyll a + a' in annual
laminations of Cores L.P.31, 32 and 35 from Loe
Pool.

Chlorophyll a + a' in Loe Pool Sediment

[Black Lamination]   [Grey Lamination]
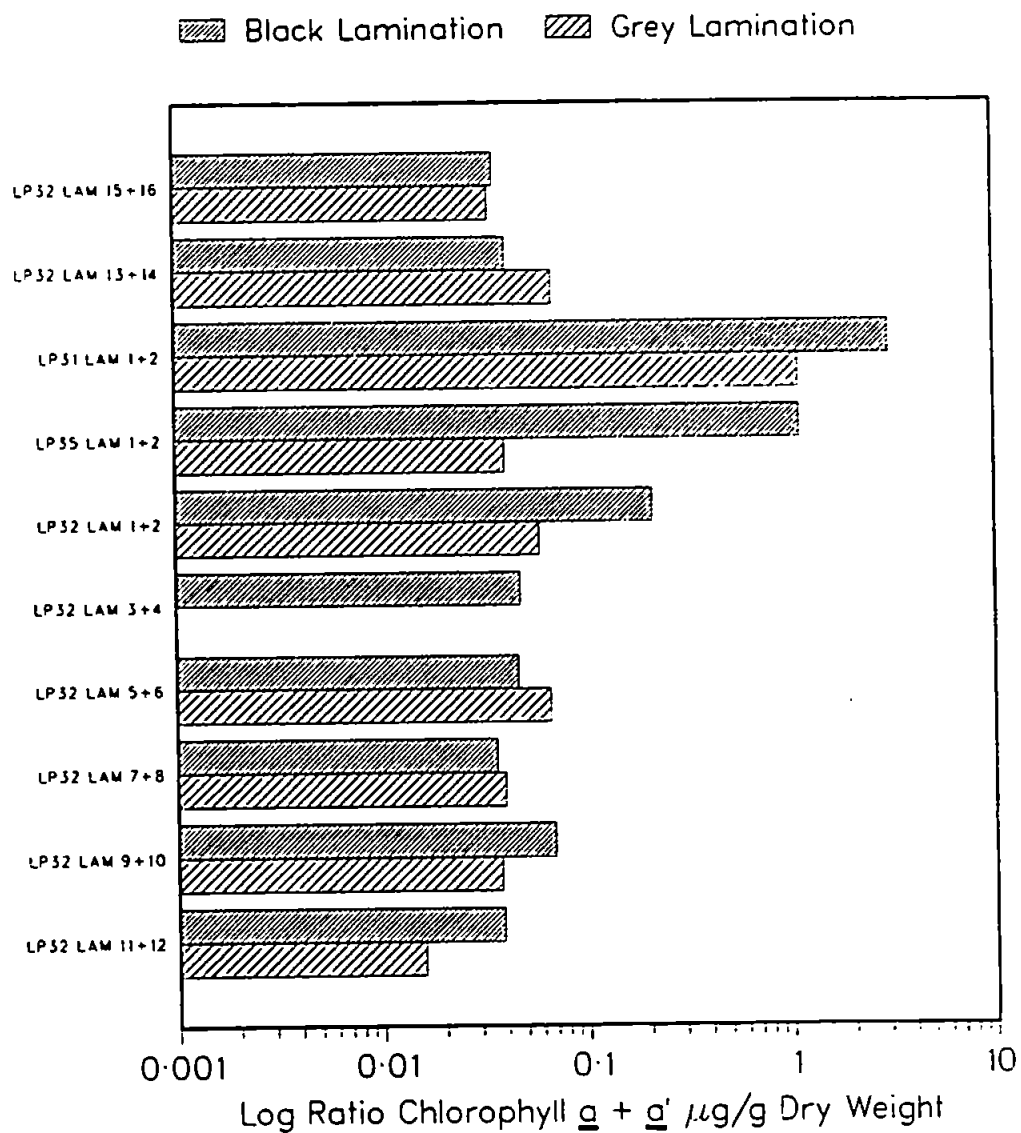
Figure 78. Concentration of Chlorophyll a + a' (log scale)
in the annual laminations of Cores L.P.31, 32 and
35 from Loe Pool.

Chlorophyll c in Loe Pool Sediment
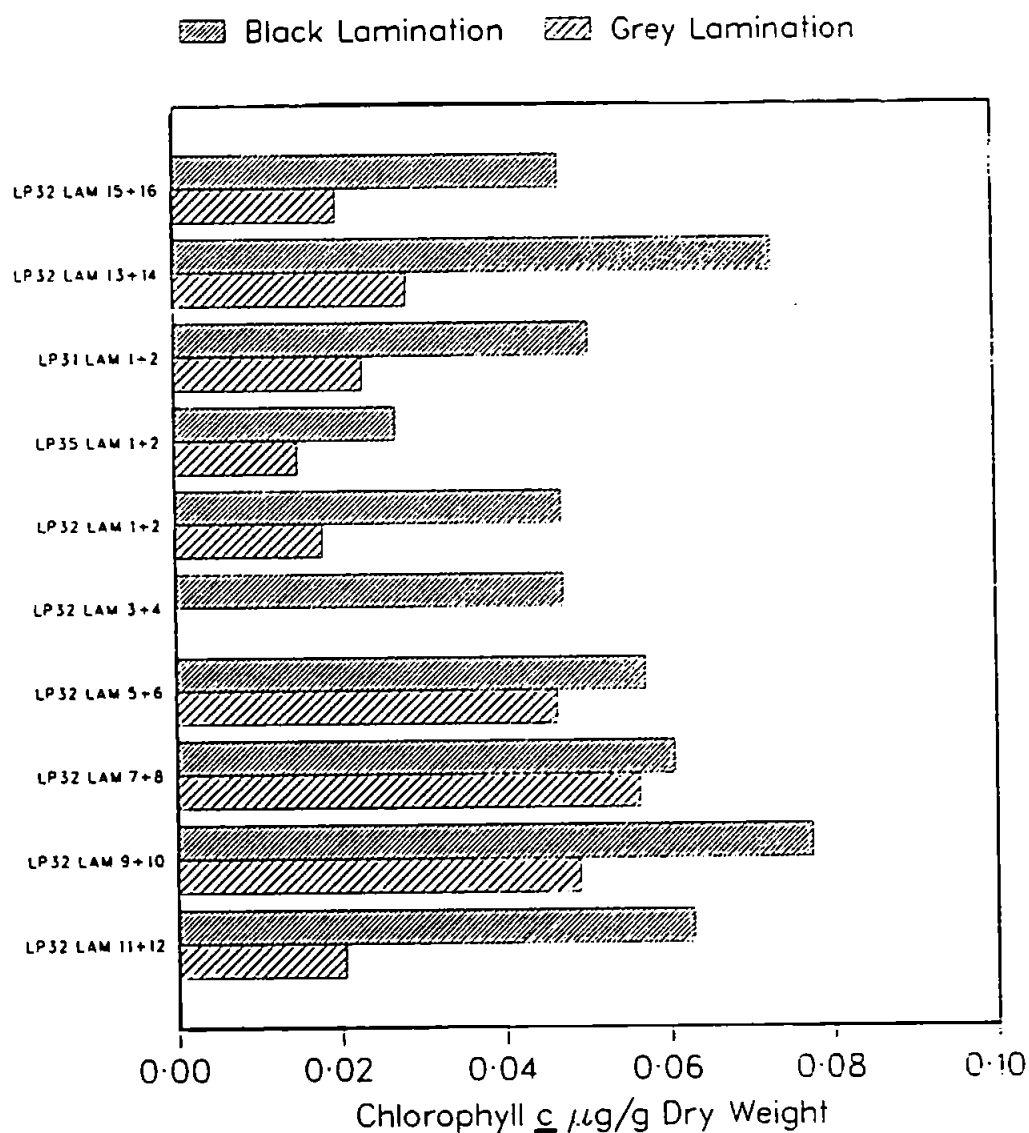
Figure 79. Concentration of Chlorophyll c in annual
laminations of Cores L.P.31, 32 and 35 from
Loe Pool.

Phaeopigments in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
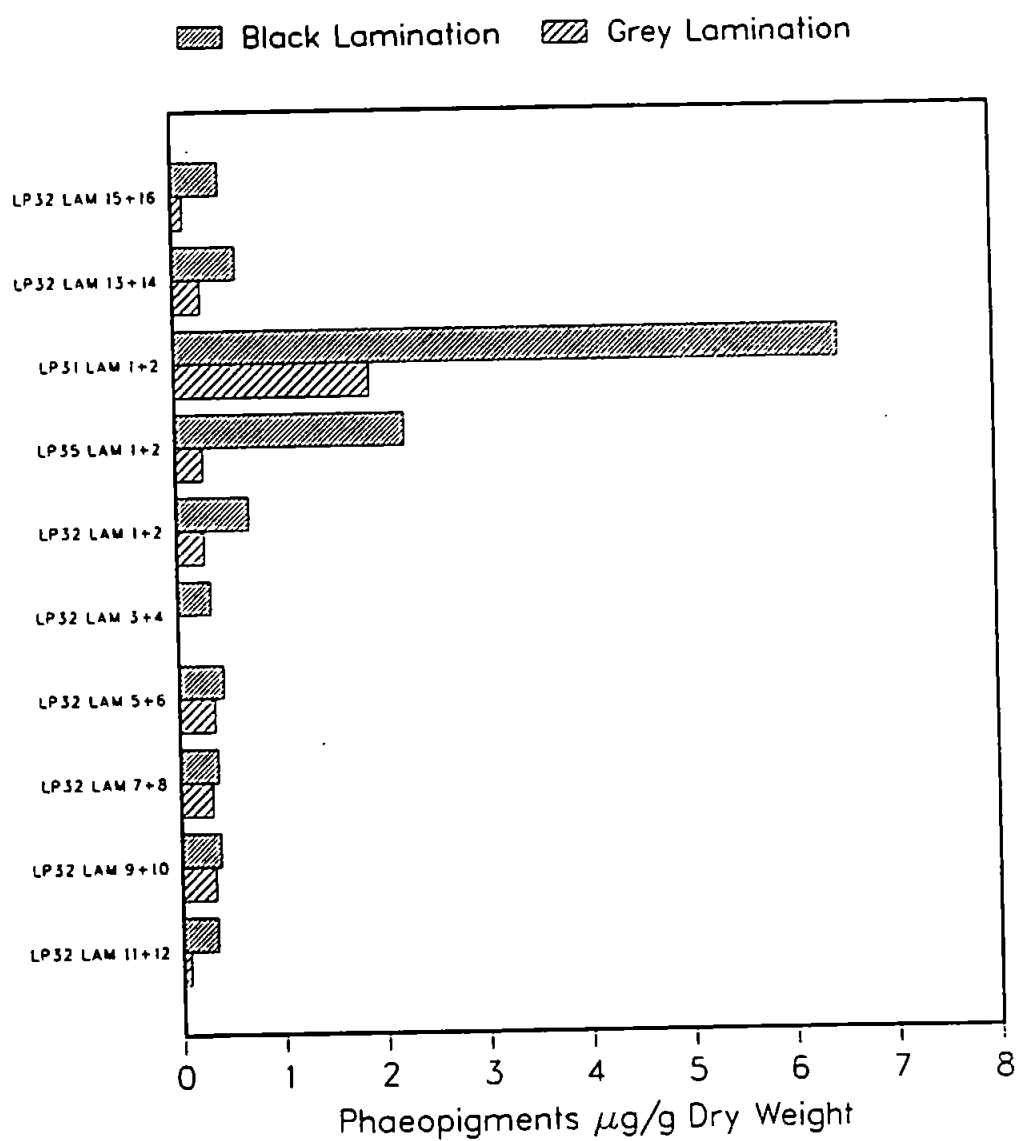
Figure 80. Concentration of Phaeopigments in annual laminations of Cores L.P.31, 32 and 35 from Loe Pool.

Phaeopigments in Loe Pool Sediment

Black Lamination ▨ Grey Lamination ▨
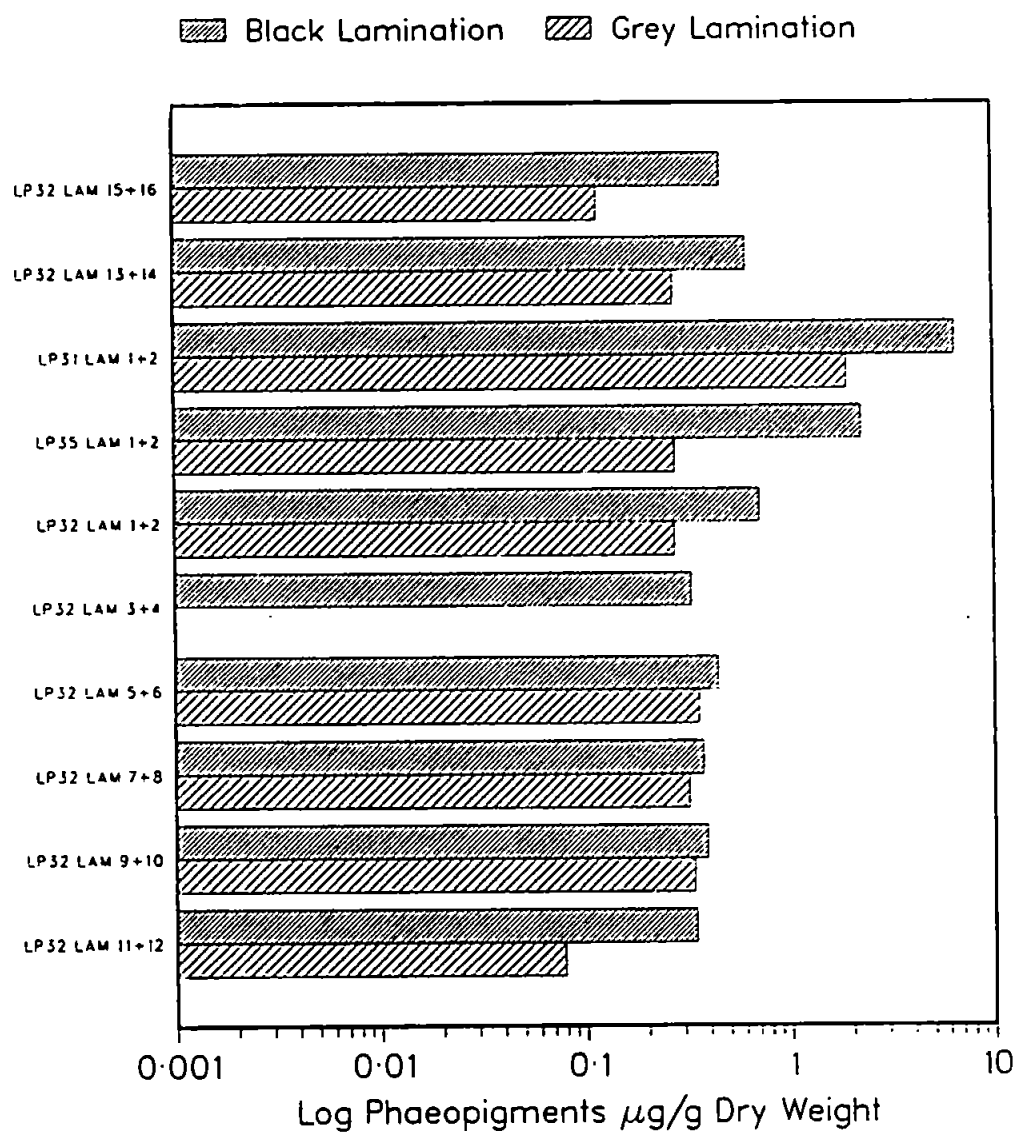
Figure 81. Concentration of Phaeopigments (log scale) in annual
laminations of Cores L.P.31, 32 and 35 from Loe Pool.

Phaeopigments : Chlorophyll a + a' in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
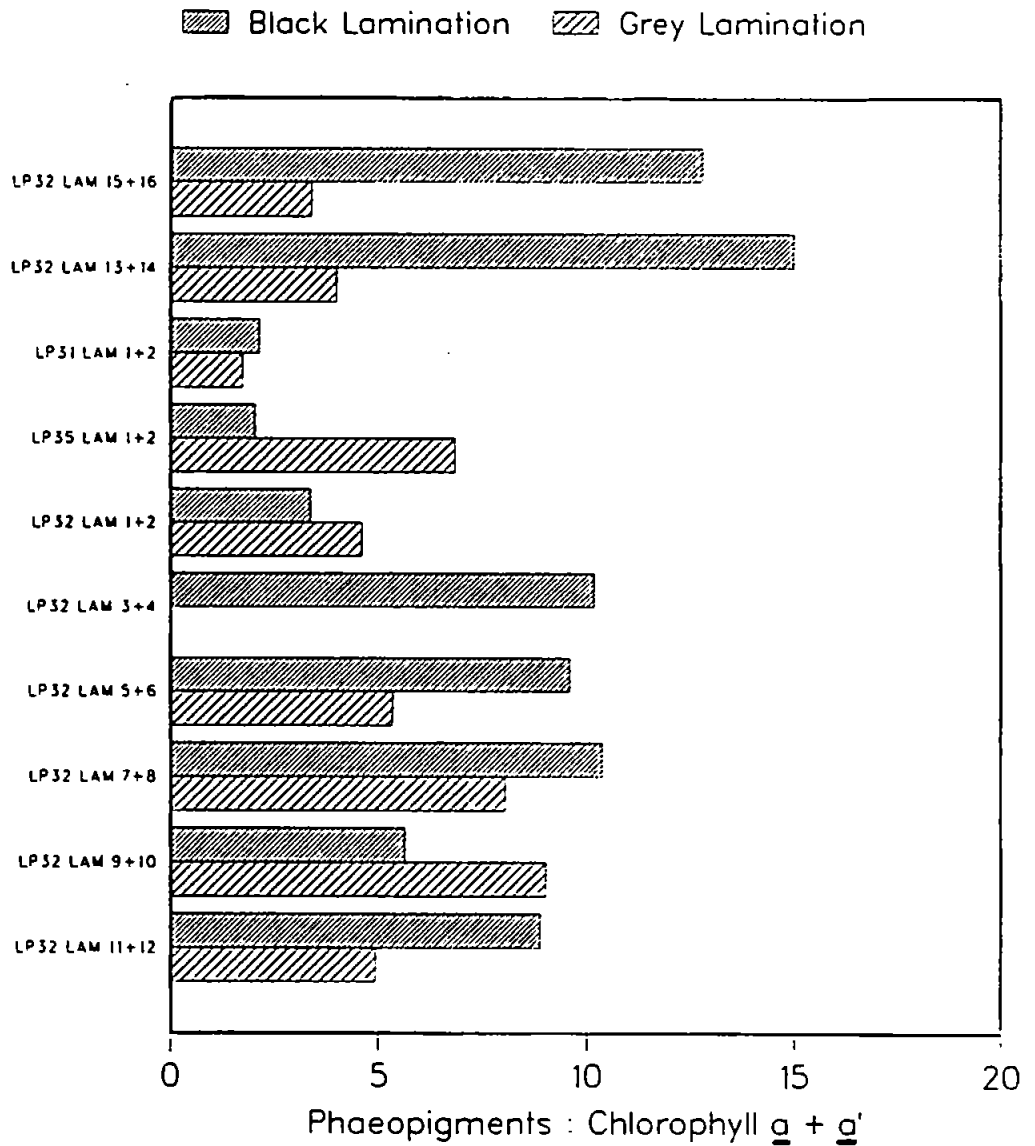
Figure 82. Ratio of Phaeopigments : Chlorophyll a + a in annual laminations of Cores L.P.31, 32 and 35 from Loe Pool.

range of the ratio is from 2-15. The average summer and winter values are 12.8 and 5.3 respectively. The ratio is higher in the black than grey lamination in six of the nine varves for which results are presented.

Only two of the carotenoid peaks could be tentatively identified; these are indicated in Figure 76. These assignments were based on retention time data and the absorbance spectra (Figs. 76, 84 & 85). Carotenoid peak 2 was considered to be lutein by comparison of the absorbance spectrum with that of a standard (Figs. 83 & 85). Carotenoid peak 1 is possibly an oxidation product of lutein. It was noted that the absorption maxima of peak 1 was 434 nm with a secondary peak at 406 nm (Fig. 84). Study of published results did not reveal any carotenoids with this spectrum. However, it was noted by Goodwin (1980) that a hypsochromic shift (shift to higher frequencies, i.e. to lower wavelengths) of 20 nm is typical of the formation of a 5,8 epoxide. There is a difference of approximately 20 nm between the absorption maxima of peak 1 and 2. In addition, as lutein is the major carotenoid present it would be reasonable to expect some degradation products of this pigment. It is, therefore, suggested that carotenoid peak 1 may be the 5,8 epoxide oxidation product of lutein.

Lutein co-eluted with the standard zeaxanthin and the oxidation product of lutein with the standard fucoxanthin. However spectra data indicated that the majority of peaks 1 and 2 were probably the oxidation product of lutein and lutein respectively.

The actual concentration of these two carotenoids was calculated according to the method described in section 4.4.7.2. The concentrations of these carotenoids in the black and grey

File   PIGMENT   Standard lutein from grass
Date
Spectrum (min):   8. 3628
Reference (min):   8. 3233
Attn (mAU):   46. 9
Absorbance (mAU) ((nm)):   40. 2 (446/ 4)
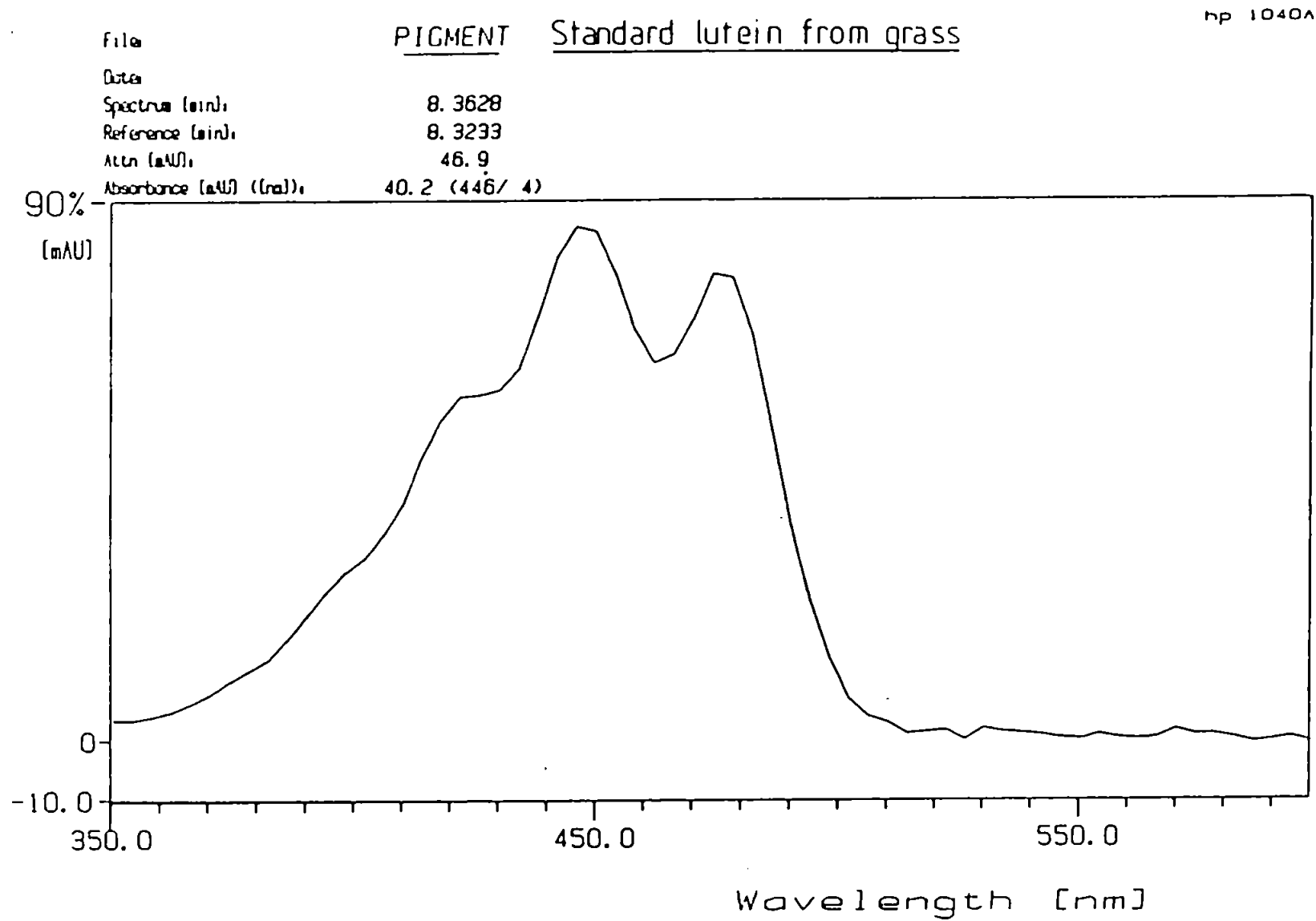
Figure 83. Absorbance scan of a lutein standard from grass.
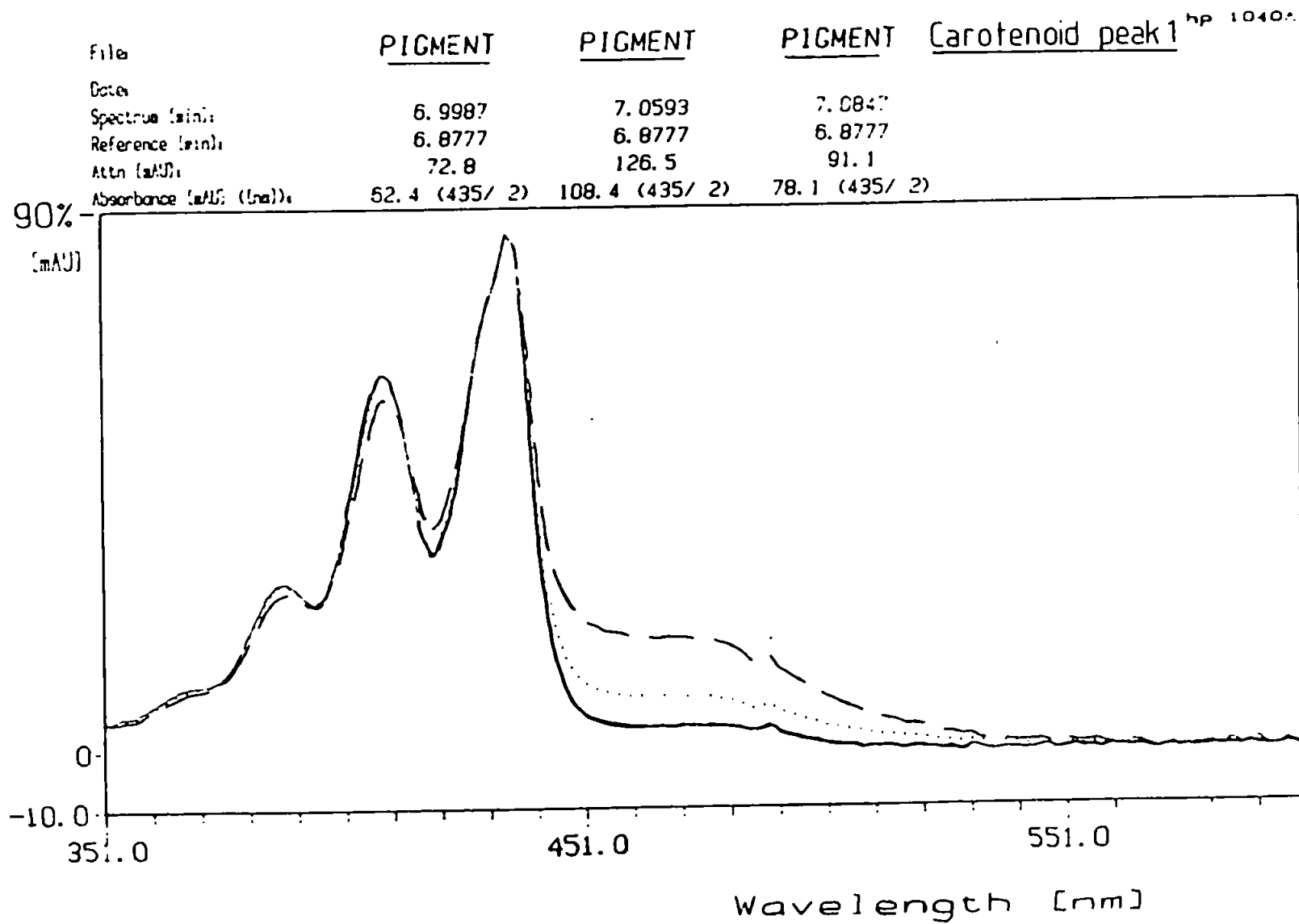
Figure 84. Absorbance scan of carotenoid peak 1.

File   PIGMENT   Carotenoid peak 2

Date
Spectrum (min):   8.4483
Reference (min):   8.3205
Attn (mAU):   77.5
Absorbance (mAU) (nm):   66.4 (451/ 2)
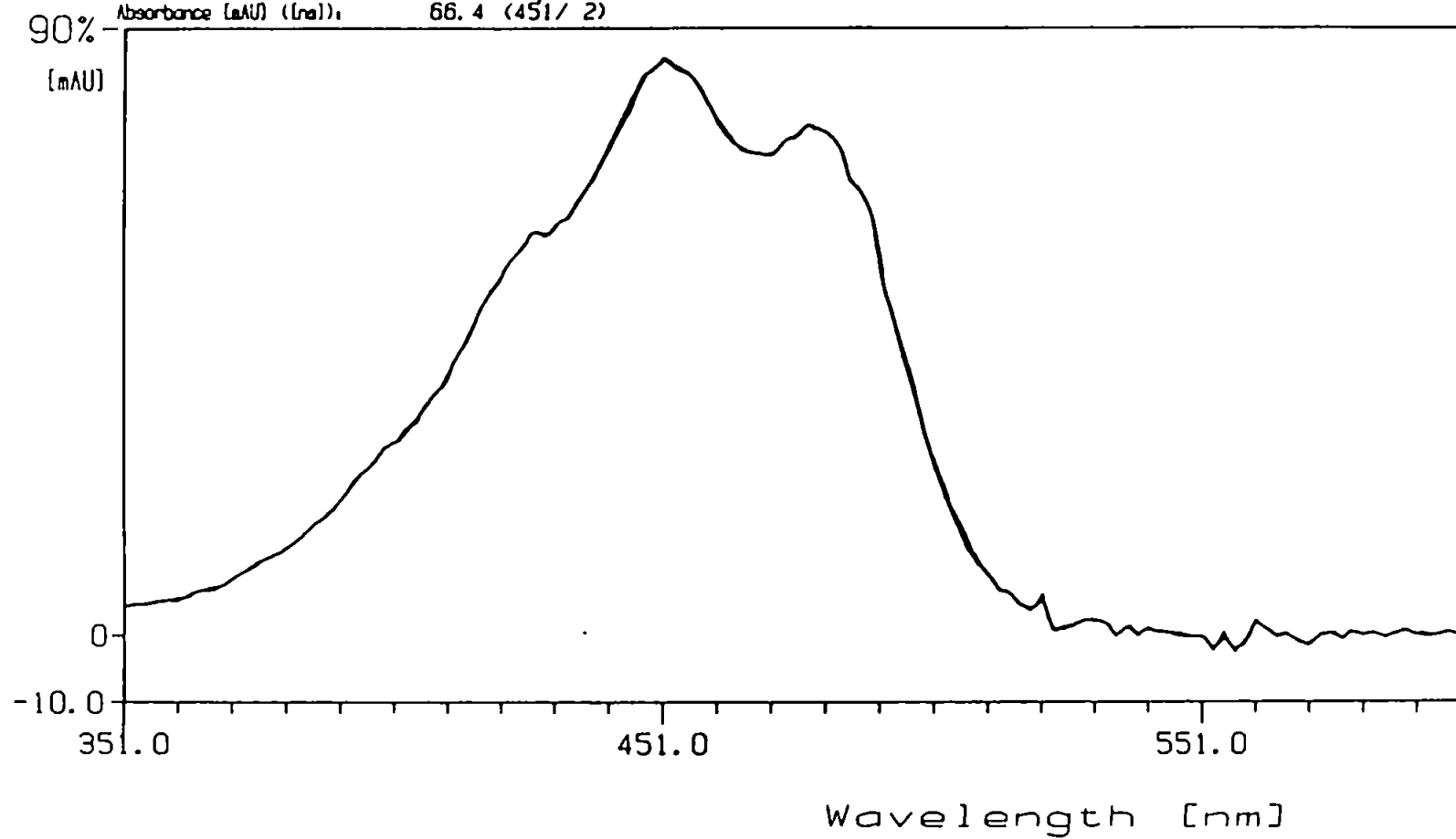
Figure 85. Absorbance scan of carotenoid peak 2.

laminations are illustrated in Figures 86 & 87. The range of peak 1 is from 0.35-0.5 µg/g dry weight. There does not appear to be any bias in distribution between black and grey laminations.

Carotenoid peak 2 has a range from 0.005-4.4 µg/g dry weight. Nine of the ten varves examined had a higher concentration of carotenoid peak 2 in the black than grey laminations.

The ratio of carotenoid peak 1:2 was calculated. This is illustrated in Figure 88. In nine of the ten varves the ratio is higher in the grey (winter) than black (summer) laminations.

5.10 Lipid Content in the Black and Grey Laminated Sediment

The total lipid extract was separated into fractions as outlined in section 4.4.8.1. All fractions were analysed by gas chromatography (G.C.) and some by computerised-gas chromatography-mass spectrometry (C.-G.C.- M.S.) Results are presented for the analysis of:

1) straight-chain hydrocarbons

2) branched/cyclic hydrocarbons

3) polynuclear aromatic hydrocarbons (P.A.H.)

4) n-alkanols

5) n-alkanoic acids

from five pairs of black and grey laminations. These were extracted from L.P.31 laminations 1 and 2, L.P.32 laminations 1 and 2, 5 and 6, 9 and 10, and L.P.35 laminations 1 and 2. Alkyl esters were not positively identified in these extracts. Chromatograms of alkyl esters are therefore included from the preliminary study of L.P.25
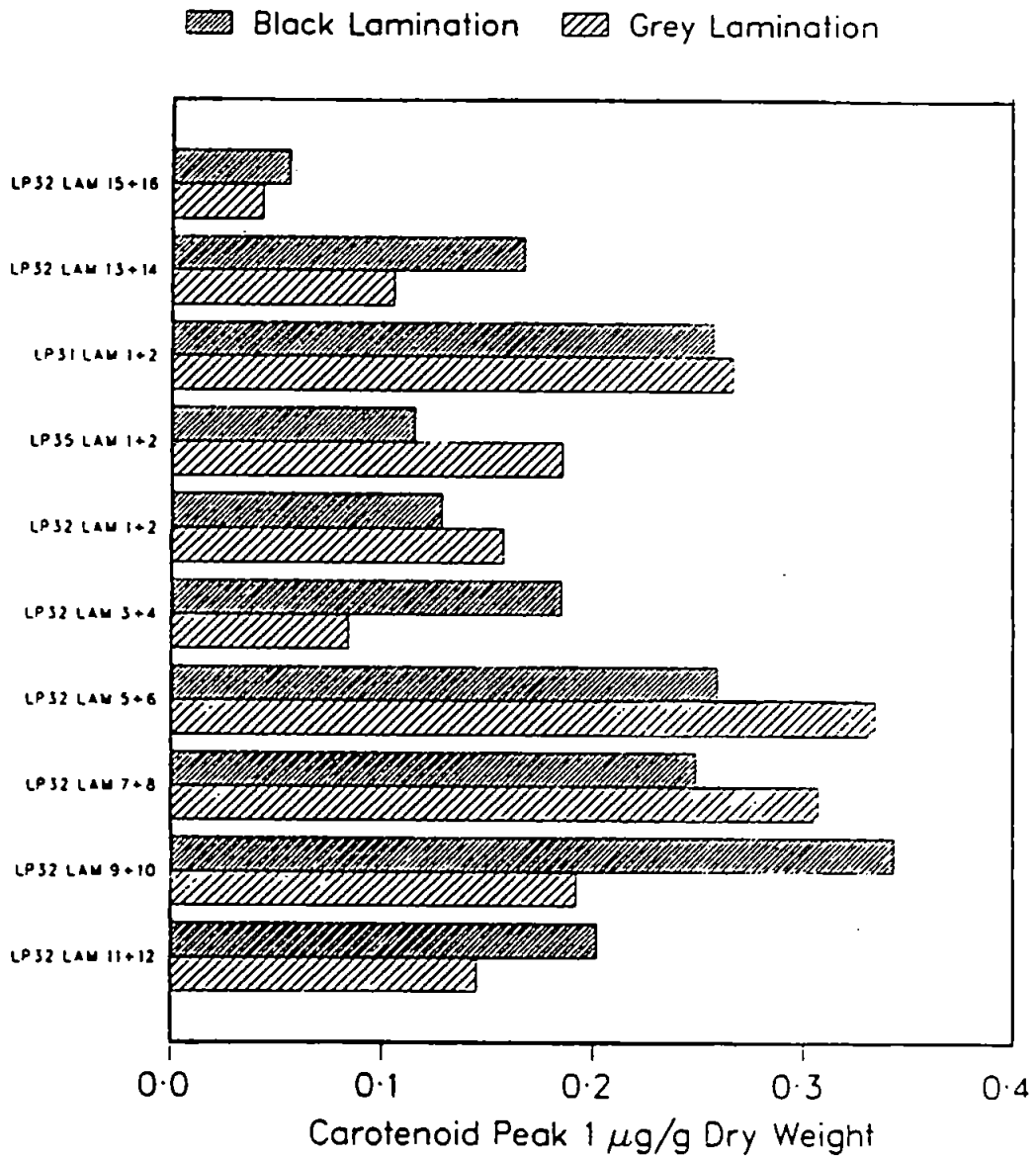
Figure 86. Concentration of carotenoid peak 1 in annual
laminations of Cores L.P.31, 32 and 35 from
Loe Pool.

Carotenoid Peak 2 in Loe Pool Sediment
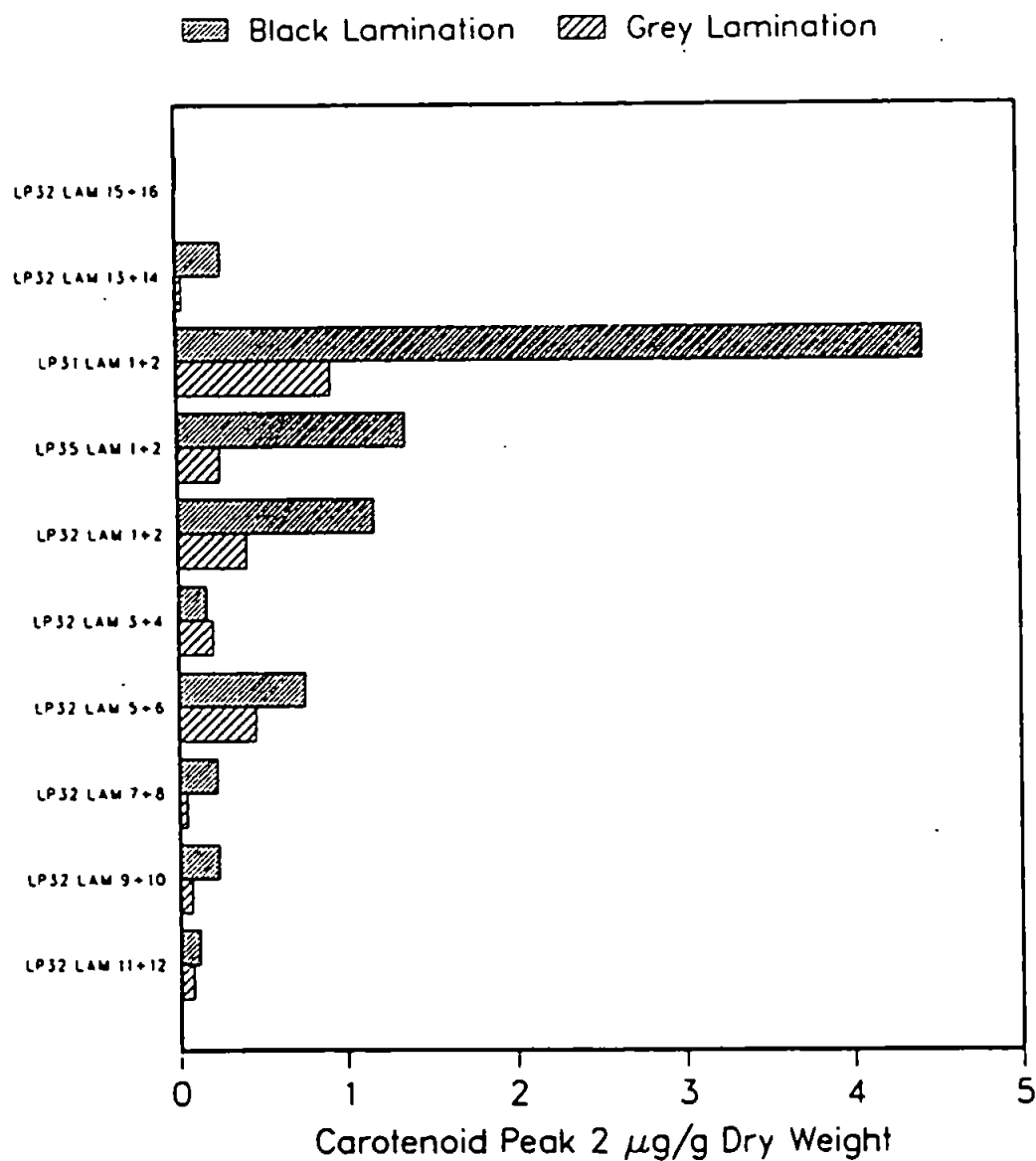
Figure 87. Concentration of carotenoid peak 2 in annual laminations of Cores L.P.31, 32 and 35 from Loe Pool.
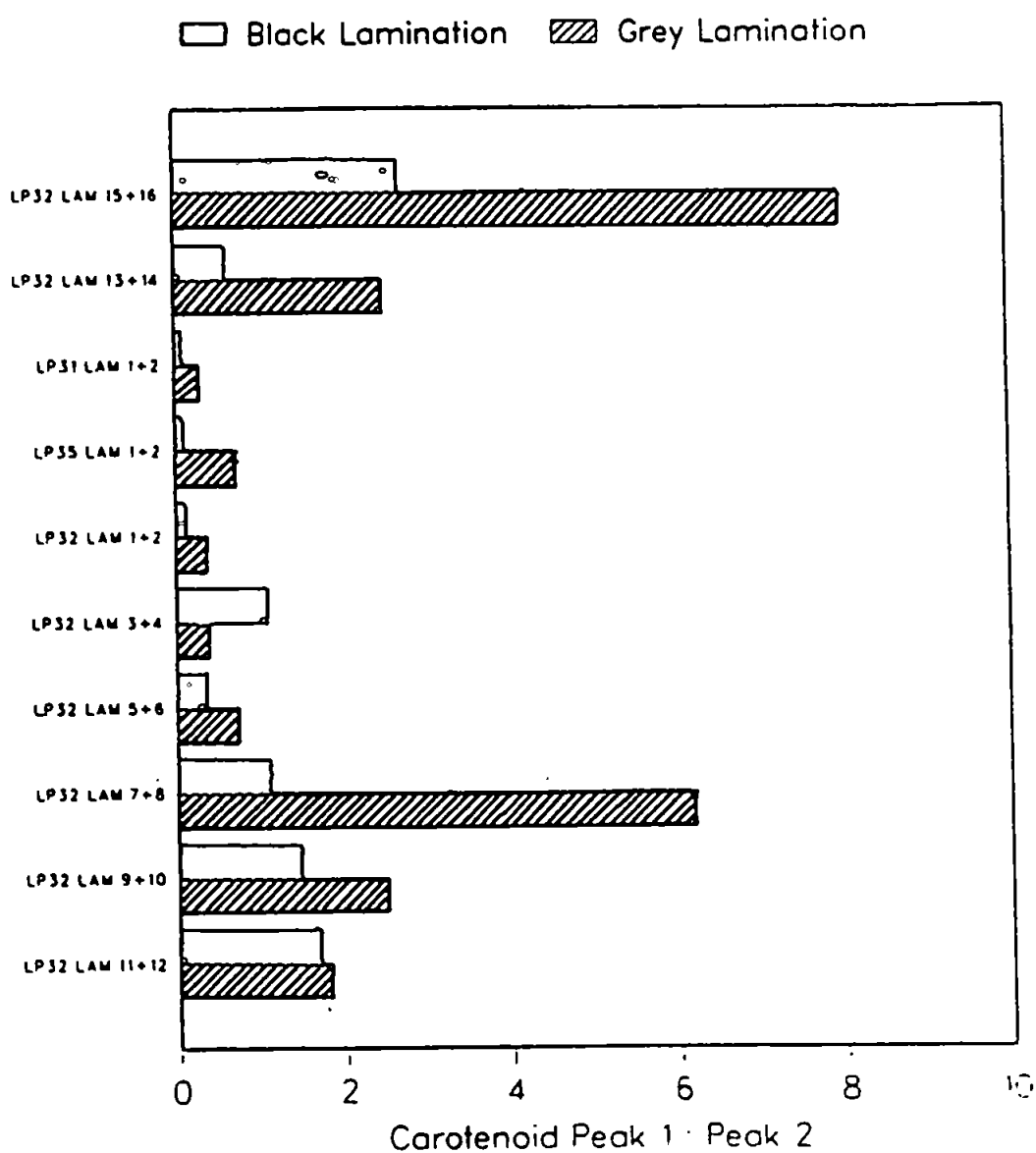
Figure 88. Ratio of carotenoid peak 1 : peak 2.

laminations 1 and 2.

For each lipid fraction a representative chromatogram is illustrated. Where possible the major peaks were identified. The three major fractions present were n-alkanols, n-alkanoic acids and n-alkanes, these all contained a homologous series. Each of these major fractions are illustrated by two pages of bar charts (for example, Figs. 93 & 94). The first page (Fig. 93) includes three pairs of black and grey laminations from cores L.P.31, L.P.32 and L.P.35 which were deposited at the same time. The second page illustrated (Fig. 94) has the results of two other black and grey laminations from core L.P.32. These were deposited two and four years prior to L.P.32 laminations 1 and 2 (Fig. 37). The bar charts on the left hand side of each page are all extracts of black (summer), and on the right hand side of grey (winter) laminations.

Lipids in the branched/cyclic hydrocarbon and aromatic fractions did not occur in a homologous series. For these compounds a typical chromatogram from one lamination is presented and relevant information from other chromatograms described.

5.10.1 Quantification of Lipid Fractions

Lipids extracted from each sediment sample were separated and analysed according to the scheme outlined in Figure 34. Each total lipid extract was found to include elemental sulphur. This sulphur formed a major part of each extract and so prevented ready quantification of each fraction by weight. Instead major components of each separated lipid fraction were quantified by comparison of their G.C. response with that of standards of a known weight.

This technique was outlined in section 4.4.8.5.

The concentration of the lipid fractions of alkanols, alkanoic acids and hydrocarbons were calculated per gramme dry weight of sediment (Table 23). It is apparent from Table 23 that there are irregular variations in the concentration of each lipid fraction between sediment deposited at the same time. In addition, there are no consistent variations of lipid concentration between the black or grey seasonal laminations.

5.10.2 Straight-Chain Hydrocarbons

A chromatogram of the pre-adduction hydrocarbon fraction from L.P.35 lamination 1 is illustrated (Fig. 89). The identification of the major peaks was based on retention time data of authentic standards. A mass fragmentogram of M/Z 85 (Fig. 90) and a mass spectrum of the largest peak (Fig. 91) confirmed these assignments. The spectrum is typical of a n-alkane, with fragments equalling the formula $C_n H_{2n} +2$. A fragmentogram of M/Z 83 confirmed the presence of alkenes, but in lower concentrations relative to the alkanes (Fig. 92).

The chromatogram of hydrocarbons (Fig. 89) has a flat baseline without any apparent "hump" of an unresolved complex mixture (U.C.M.). The concentration of n-alkanes with carbon numbers 17 to 33 was calculated for each extract analysed. These are presented as a % of the total alkanes (Figs. 93 & 94). The carbon preference index (C.P.I.) was calculated for each extract. This figure is given on each bar chart.

The bar charts (Figs. 93 & 94) all show a similar pattern. The

Quantification of lipids from Loe Pool Sediment mg/g dry weight					
Core	Colour of core	alkanes	alkanols	alkanoic acids	perylene
LP 31 lam 1	black	9.988×10^{-3}	0.0221	0.0198	lost sample
LP 31 lam 2	grey	7.116×10^{-3}	0.0038	0.0031	1.47×10^{-5}
LP 35 lam 1	black	11.75×10^{-3}	0.330	0.0199	40.7×10^{-5}
LP 35 lam 2	grey	0.177×10^{-3}	0.044	0.1165	37.2×10^{-5}
LP 32 lam 1	black	4.947×10^{-3}	0.0488	0.00022	61.5×10^{-5}
LP 32 lam 2	grey	8.951×10^{-3}	0.0237	0.00053	0.564×10^{-5}
LP 32 lam 5	black	10.425×10^{-3}	0.011	0.0409	115.8×10^{-5}
LP 32 lam 6	grey	8.15×10^{-3}	0.0068	0.0219	62.03×10^{-5}
LP 32 lam 9	black	3.169×10^{-3}	0.0046	0.0084	40.88×10^{-5}
LP 32 lam 10	grey	15.423×10^{-3}	0.0344	0.0211	180.6×10^{-5}

Table 23. Quantification of lipids extracted from the black/grey laminated sediment formed in Loe Pool.
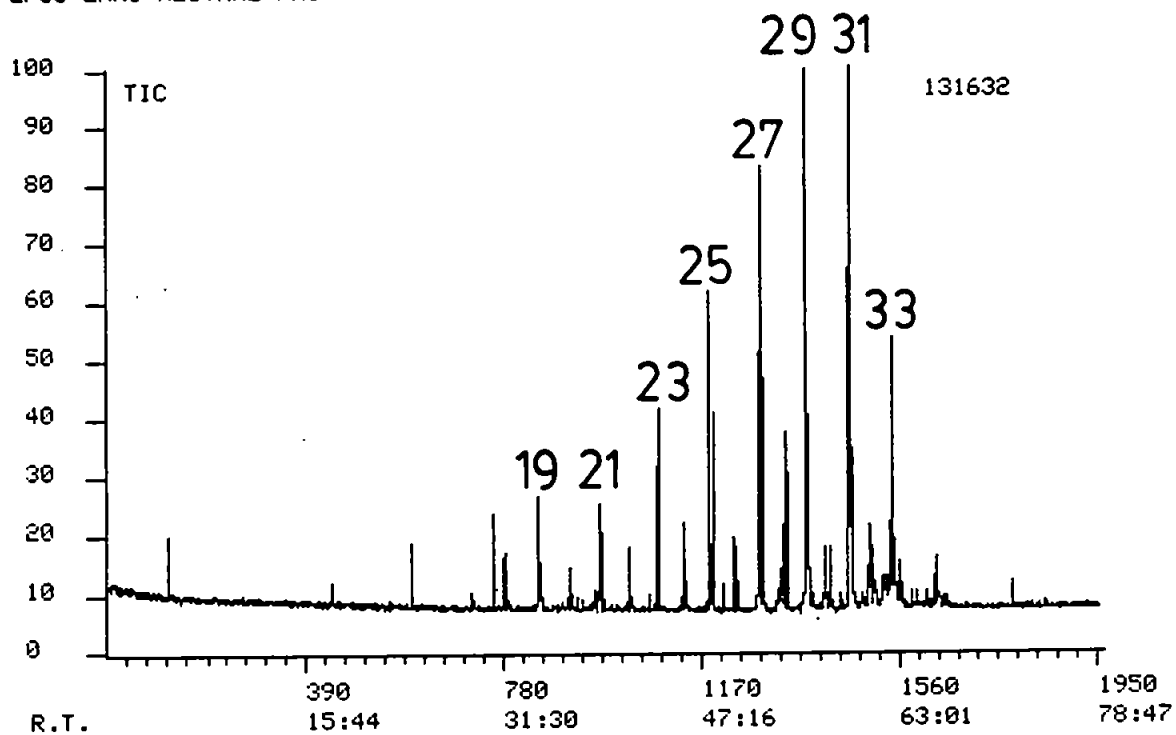
Figure 89. Total ion chromatogram of hydrocarbons, numbers
indicate n-alkanes (for conditions of analysis
see section 4.4.8.3).
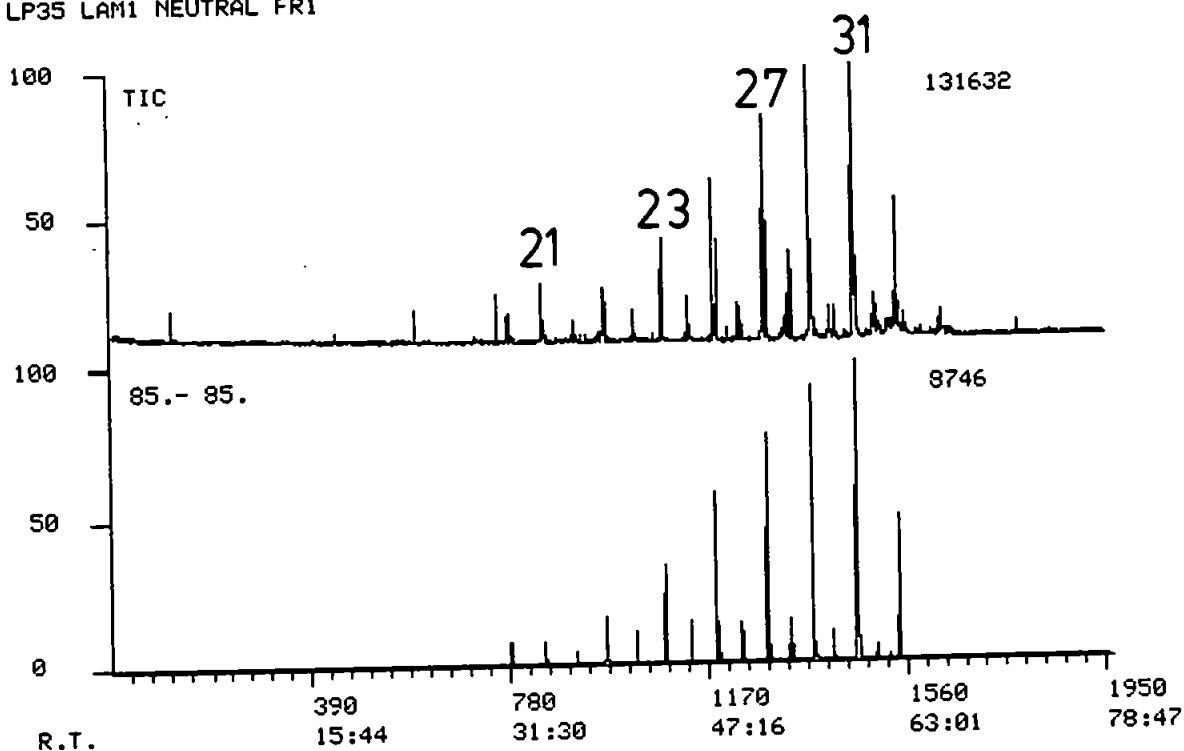
Figure 90. M/Z 85 Mass Fragmentogram of hydrocarbons, numbers indicate n-alkanes (for conditions of analysis see section 4.4.8.3).

Figure 91. Mass Spectrum of C 31 n-alkane, fragments indicate a
n-alkane (for conditions of analysis see section 4.4.8.3).
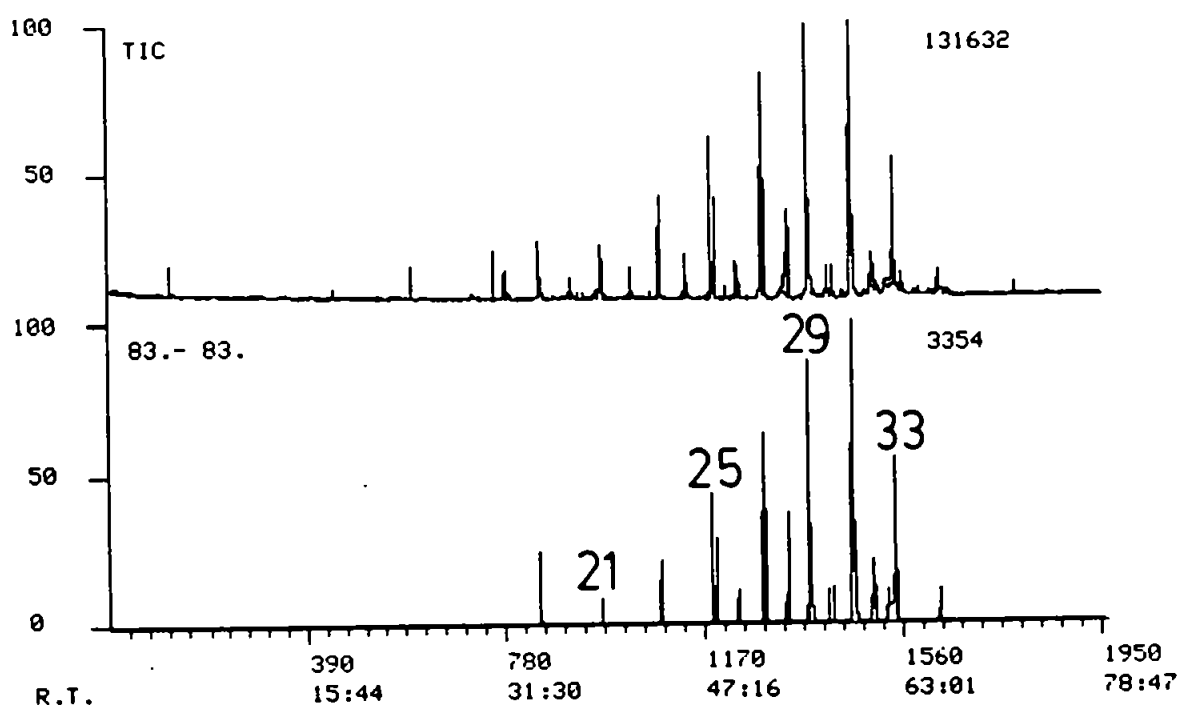
Figure 92. M/Z 83 Mass Fragmentogram of hydrocarbons, numbers indicate n-alkenes (for conditions of analysis see section 4.4.8.3.).
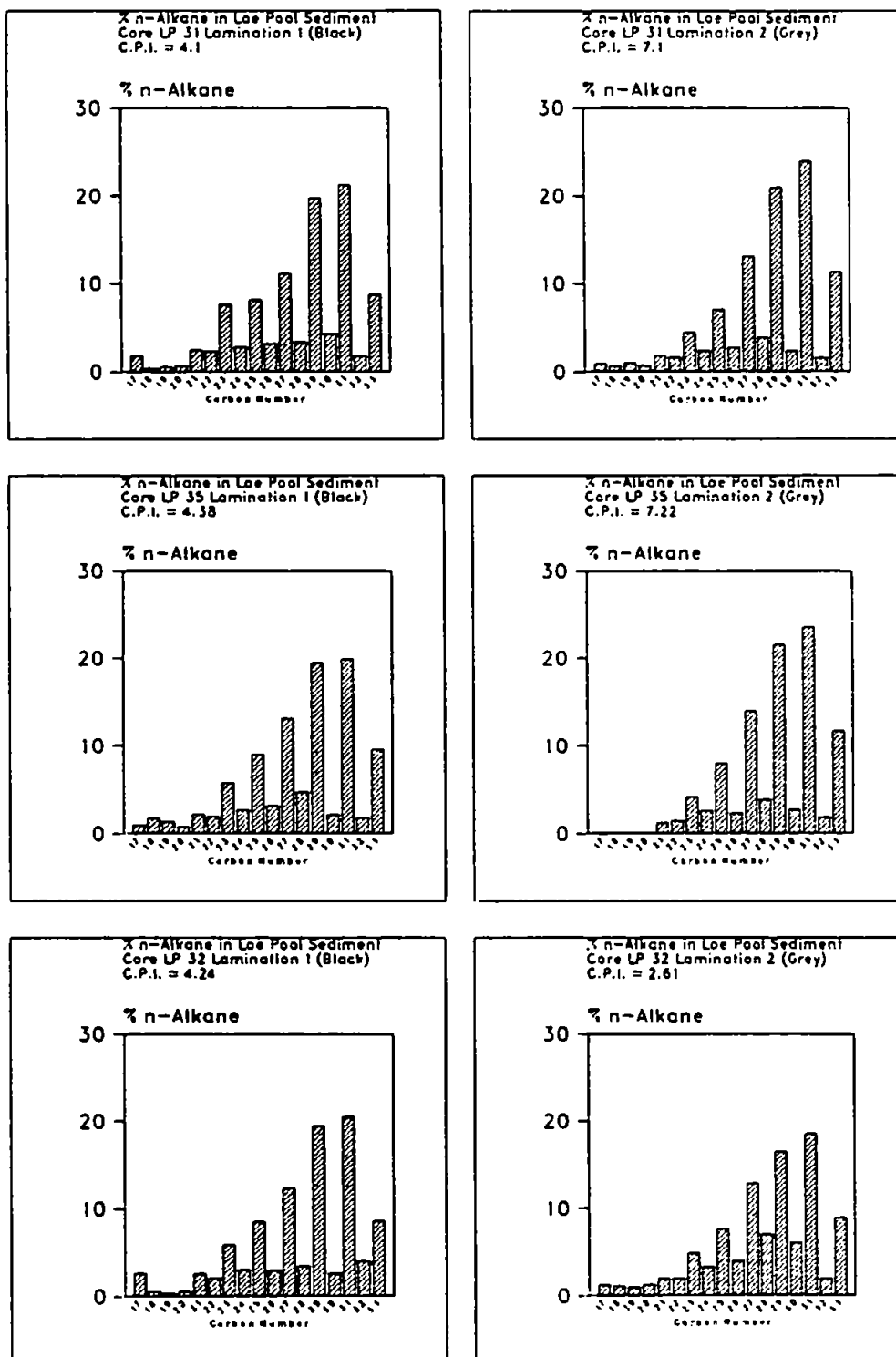
Figure 93. Distribution of n-alkanes in Cores L.P.31, 32 and 35, laminations 1 and 2, from Loe Pool.
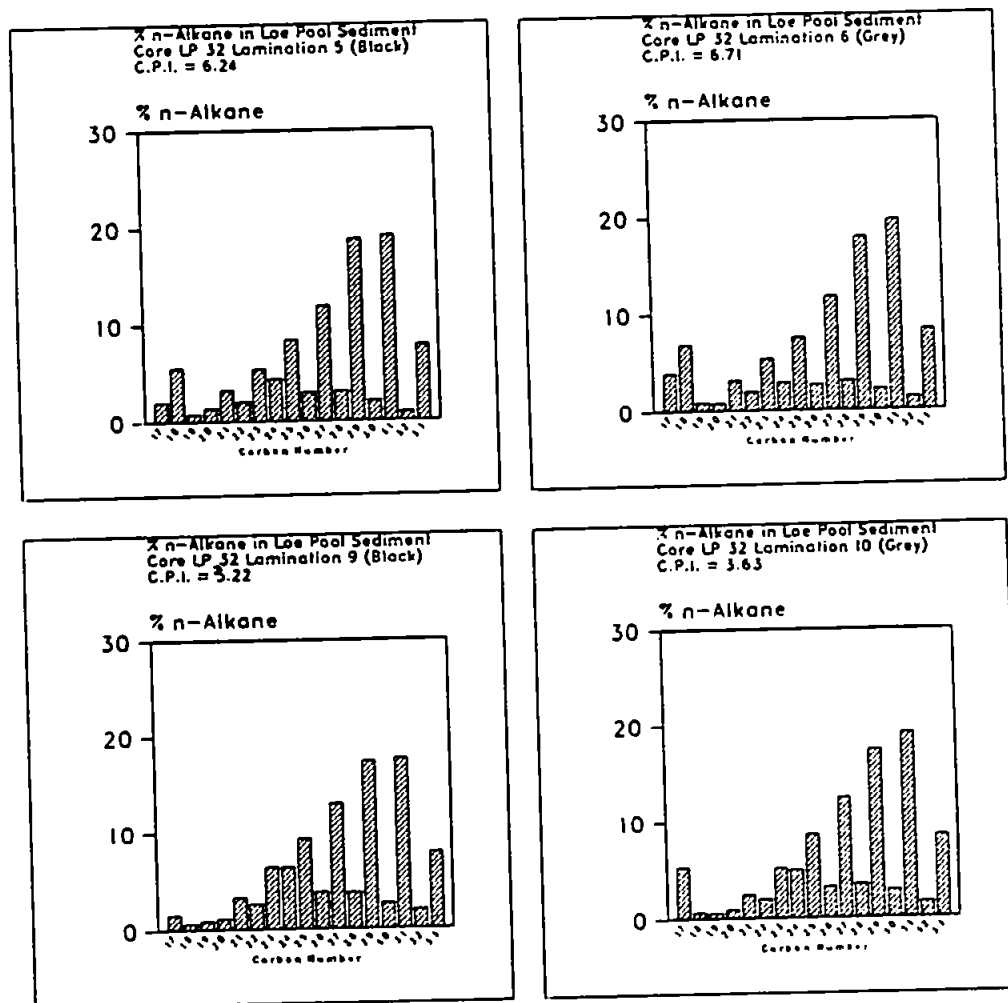
Figure 94. Distribution of n-alkanes in L.P.32 laminations
5, 6, 9 and 10 from Loe Pool.

range is dominated by a mode maximising at n-C 31. Most of the extracts exhibit a secondary mode around n-C 17 and n-C 18. Each extract has an odd over even predominance with a C.P.I. range from 2.61-7.22.

The black and grey laminations may be differentiated according to C.P.I. values. The C.P.I. is higher in the grey lamination of four of the five varves examined. The average C.P.I. of the black sediment is 4.4 compared with 5.4 in the grey layers.

5.10.3 Branched and Cyclic Hydrocarbons

The hydrocarbon fraction, comprising principally of alkanes and alkenes, was separated into straight-chain components and branched/cyclic hydrocarbons by the technique of urea adduction (section 4.4.8.1). The chromatograms of each non-adducted hydrocarbon fraction (branched/cyclic lipids) were similar. An example of the total ion chromatogram of this fraction from L.P.32 lamination 5 is illustrated (Fig. 95). The peaks labelled 1 and 2 were thought to be pristane and phytane respectively from retention time data. However partial fragmentograms of M/Z 83 and M/Z 85 (Figs. 96 & 97) indicated the presence in peaks 1 and 2 of unsaturated compounds in addition to alkanes.

The mass spectrum of peak 1 is illustrated in Figure 98 together with the mass spectrum of authentic pristane (Fig 99). The mass spectrum of peak 1 (Fig. 98) does not appear to be pristane (Fig. 99); the distinctive ion at 183 is missing. However, the peak is similar to the mass spectrum of a C 20 branched alkane considered

Figure 95. Total Ion Chromatogram of hydrocarbon non-adduct
from L.P.32 lam 5 from Loe Pool (Conditions see
section 4.4.8.3.).

Figure 96. M/Z 83 Mass Fragmentogram of hydrocarbon non-adduct fraction (for conditions of analysis see section 4.4.8.3.).
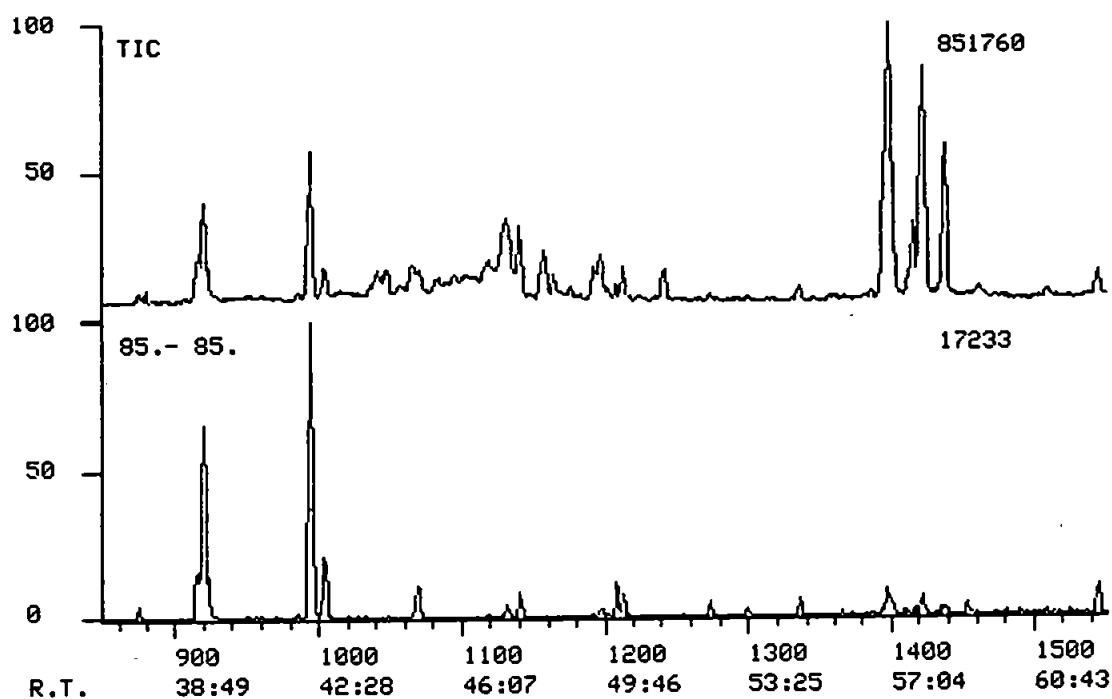
Figure 97. M/Z 85 Mass Fragmentogram of hydrocarbon non-adduct
        fraction (for conditions of analysis see section
        4.4.8.3.).

Figure 98. Mass Spectrum of peak 1 from hydrocarbon non-adduct
(for conditions of analysis see section 4.4.8.3.).

Figure 99. Mass Spectrum of authentic pristane
(from Robson, pers. comm.).

to be 2,6,10- trimethyl-7(3-methylpentane)dodecane (Yon, 1982; Rowlands et al. 1986). The compound is characterised by a doublet at M/Z 168/169 which is typical of authentic 2,6,10-trimethyl-7(3-methylpentane)dodecane as synthesised by Robson (pers. comm.) (Fig. 100).

The mass spectrum of peak 2 and a spectrum of authentic phytane are illustrated (Figs.101 & 102). The two compounds are clearly not the same. Peak 2 does not contain the M/Z 197 ion which is characteristic of phytane. The presence in the mass spectrum of M/Z 210 (equivalent of C 15 H 30 compounds) suggests the occurrence of co-eluting phytenes and possibly phytadienes.

Peaks 3 and 4 in the chromatogram (Fig. 95) were considered by retention time data and comparison with published results (Jones, 1986) to be hopanoids. A mass fragmentogram of M/Z 191 confirms the presence of these compounds (Fig. 103). The mass spectrum of peaks 3 and 4 are shown in Figures 104 and 105. The molecular ions of 410 and 426 are consistent with a C 30 hopene and C 31 hopane respectively (Fig. 106).

5.10.4 Alkyl Esters

Alkyl esters were isolated from laminations 1 (black) and 2 (grey) from core L.P.25. The chromatograms are shown in Figure 107. The identification of each peak was noted on the chromatograms. These were assigned by retention time data (Cranwell pers. comm.). Each extract had a range of n-C 34 to n-C 48 alkyl esters. In addition, the sediment deposited in the grey lamination contained a suite of
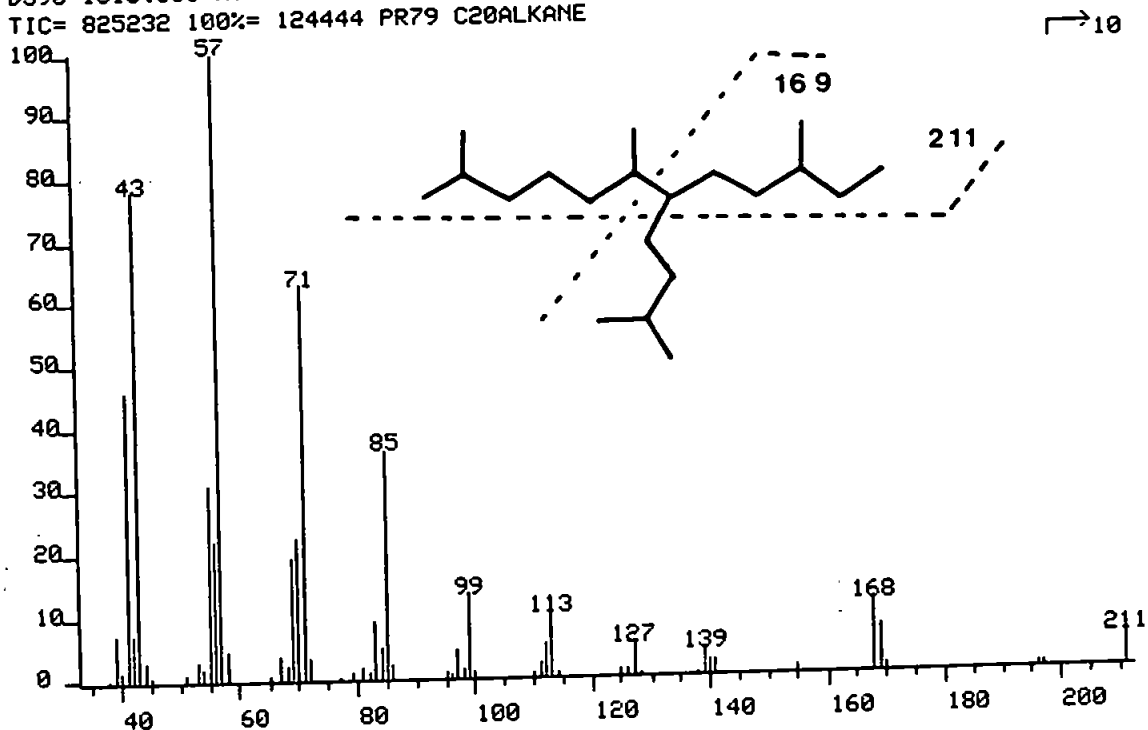
Figure 100. Mass Spectrum of authentic 2,6, 10-trimethyl-7 (3-methyl pentane) dodecane (from Robson Ph.D. thesis in preparation).

Figure 101. Mass Spectrum of peak 2 from hydrocarbon non-adduct
(for conditions of analysis see section 4.4.8.3.).

Figure 102. Mass Spectrum of authentic phytane
(from Robson, per. comm.).

Figure 103. M/Z 191 Mass Fragmentogram of hydrocarbon non-adduct
fraction (for conditions of analysis see section
4.4.8.3.).

Figure 104. Mass Spectrum of peak 3 from hydrocarbon non-adduct
        fraction (for conditions of analysis see section
        4.4.8.3.).

Figure 105. Mass Spectrum of peak 4 from hydrocarbon non-adduct
fraction (for conditions of analysis see section
4.4.8.3.).

Figure 106. Generalised structure of C 31 hopane with carbon
numbers and characteristic M/Z 191 fragmentation.

	formula	molecular weight
C 31 hopane	C31 H56	426
C 30 hopane	C30 H52	412
C 30 hopene	C30 H50	410
(1 degree unsaturation)		
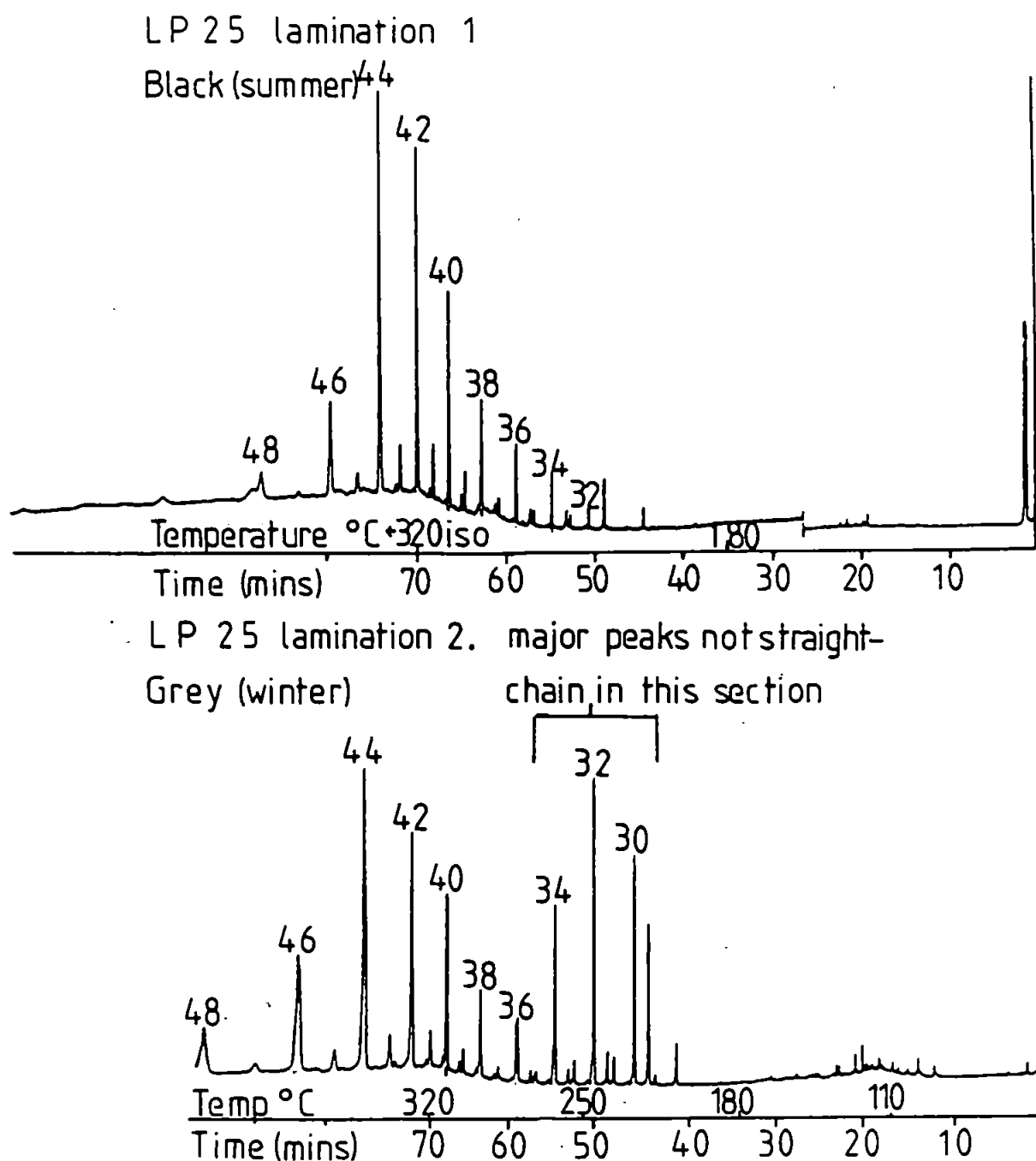
Figure 107. Chromatogram of alkyl esters from Core L.P.25
laminations 1 and 2. Numbers indicate carbon
numbers of n-alkyl esters (for conditions
see section 4.4.8.2).

C 28-C 34 branched alkyl esters. There is an even over odd
dominance, though this was not quantified.

5.10.5 Alkanols

Alkanols from each lipid extract were converted to their
T.M.Si-ethers with B.S.T.F.A. and analysed by G.C. (section
4.4.8.1). A chromatogram of the extract from L.P.32 lamination 2
(grey) is illustrated (Fig. 108). Peaks were identified on the
basis of retention time data of authentic standards and
C.-G.C.-M.S. information. The mass spectrum of the major peak in
the alkanol extract of L.P.32 lamination 2 is shown (Fig. 109). The
spectrum has a strong molecular ion minus methyl group (M-15) and
was identified as n-C 26 alkanol.

The chromatogram (Fig. 108) has evidence of sedimentary sterols.
More information concerning the distribution of sterols in Loe Pool
sediment is given by Eglinton (1982). The range of n-alkanols in
most of the lipid extracts is from C 14 to C 32. The concentration
of the C 14 to C 28 n-alkanols in each black and grey lamination is
illustrated in Figures 110-111. Each chromatogram has a unimodal
distribution around n-C 26 and a high even over odd predominance.
There were two factors that distinguished the black from grey
sediment. Firstly, that the C.P.I. is higher in four of the black
than grey laminations. Secondly, the C 26:C 28 n-alkanol ratio is
higher in the black layer of each varve (Table 24).
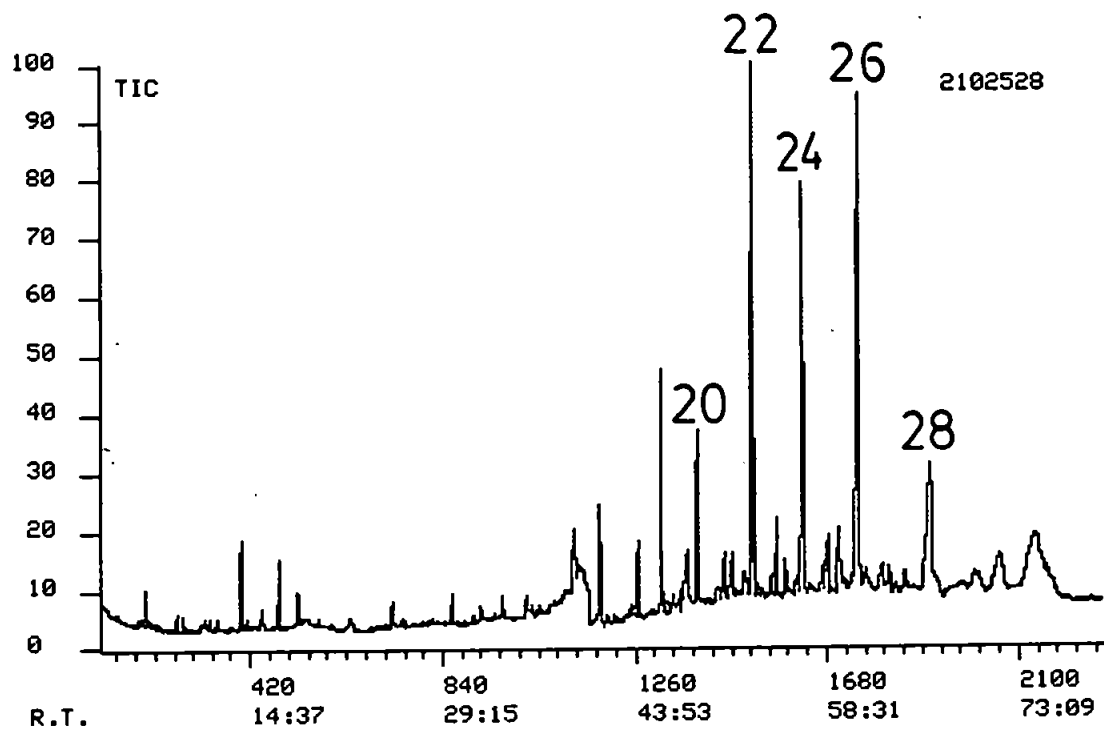
Figure 108. Total ion chromatogram of T.M.Si. Alkanols,
numbers indicate carbon number of n-alkanols
(for conditions of analysis see section 4.4.8.3.).
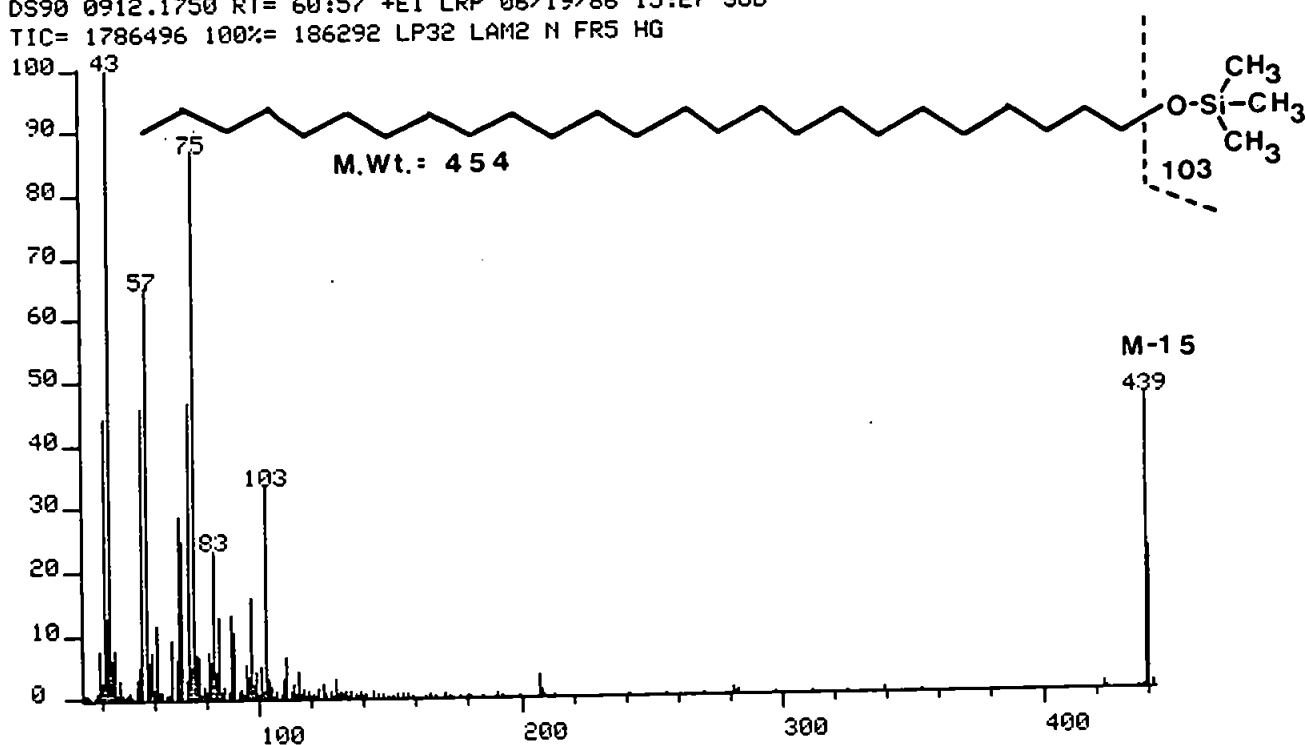
Figure 109. Mass Spectrum of C26 TMSi n-alkanol (for conditions
of analysis see section 4.4.8.3.).
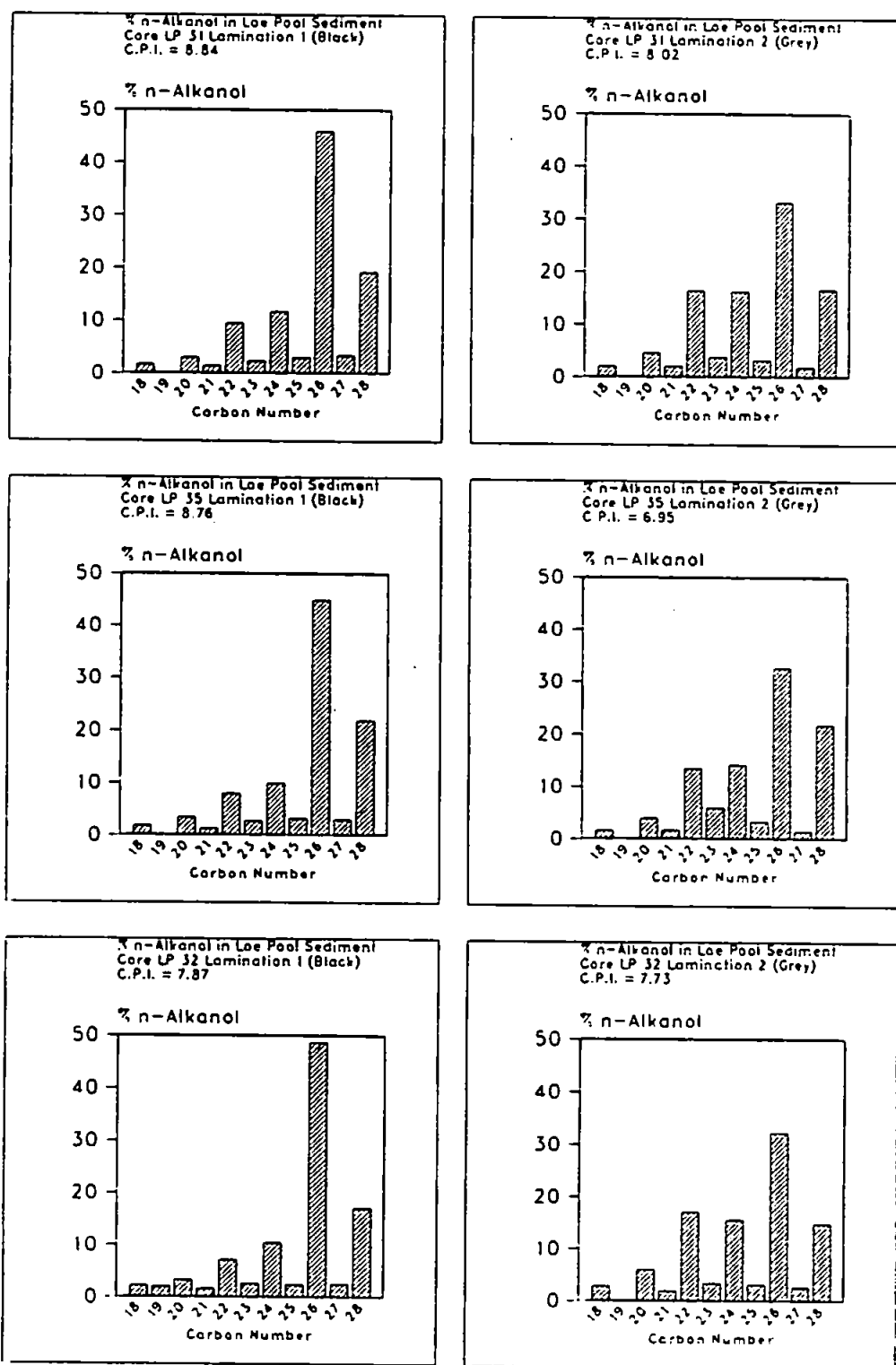
Figure 110. Distribution of n-alkanols in L.P.31, 32 and 35
laminations 1 and 2 from Loe Pool.

Figures 111. Distribution of n-alkanols in L.P.32
laminations 5, 6, 9 and 10 from Loe Pool.

Sediment fraction	Colour of sediment	Ratio $C_{26}:C_{28}$ n-alkanol
LP 31 lam 1	black	2.38
LP 31 lam 2	grey	2.0
LP 35 lam 1	black	2.64
LP 35 lam 2	grey	1.49
LP 32 lam 1	black	2.84
LP 32 lam 2	grey	2.16
LP 32 lam 5	black	2.5
LP 32 lam 6	grey	2.2
LP 32 lam 9	black	2.17
LP 32 lam 10	grey	1.73

Table 24. Ratio $C_{26}:C_{28}$ n-alkanols in Loe Pool sediment.

5.10.6 Polynuclear Aromatic Hydrocarbons

The chromatograms of the polynuclear aromatic hydrocarbon (P.A.H.) fractions from each extract were all similar. An example is given in Figure 112. Each chromatogram was dominated by one component, the mass spectrum of which is illustrated (Fig. 113). The compound has a molecular ion at M/Z 252 and a fragment ion at M/Z 126. It was identified as perylene. Other P.A.H. detected by G.C. analysis were not present in sufficient concentrations for identification by C.-G.C.-M.S.

The concentration of perylene was calculated for each fraction analysed. The results are presented in Figures 114 and 115. In three of the four varves for which there are results, there was a higher concentration of perylene per gramme dry weight in the black than grey lamination.

5.10.7 Alkanoic Acids

The total lipid extract was initially separated into acid and neutral fractions according to the saponification technique outlined in section 4.4.8.1. The total acid fraction was derivatised with B.S.T.F.A. prior to analysis. The acid fraction from each lamination was analysed by G.C., an example is the acid fraction of L.P.35 lamination 2 (Fig. 116). Peaks were identified by comparison of retention time data of authentic standards. These assignments were confirmed by C.-G.C.-M.S. data.

The mass spectrum of the major peak is shown (Fig. 117). The

DS-90 CHROMATOGRAM REPORT RUN: 0932   6/26/86 15:27
LP32 LAM 10 FR1B
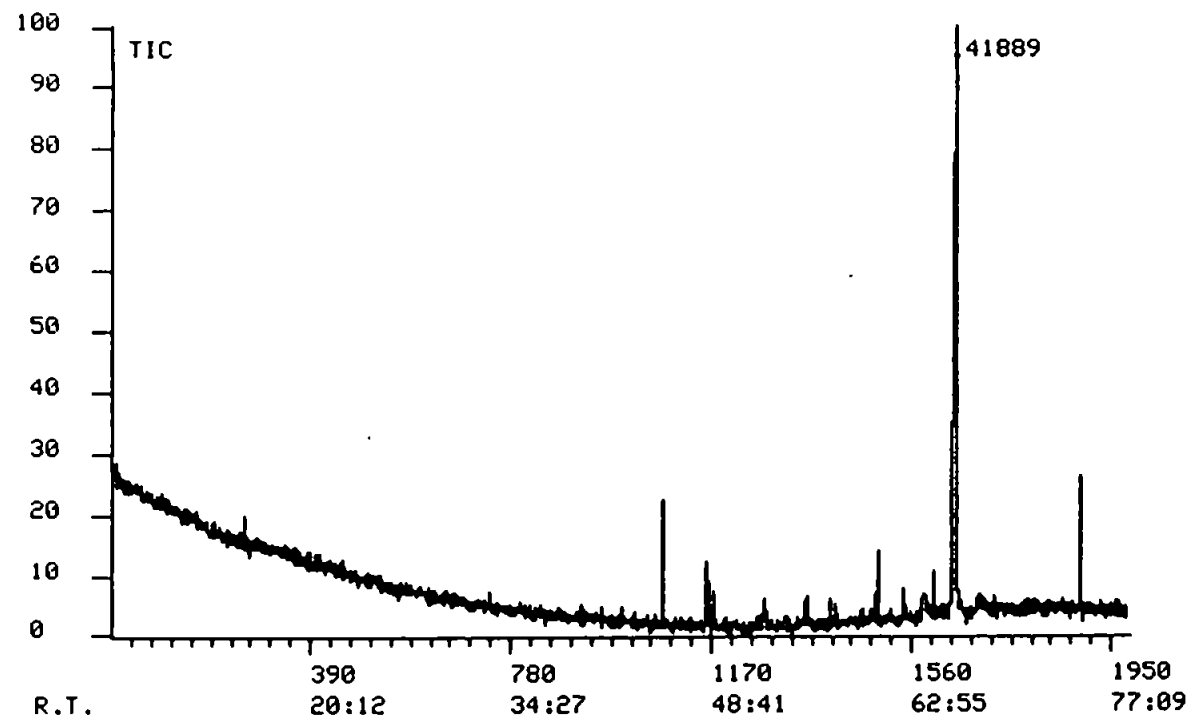
Figure 112. Total ion chromatogram of an aromatic fraction
           from Core L.P.32 lamination 10 from Loe Pool
           (for conditions see section 4.4.8.3.).

EXACT NOMINAL MULTIPLET REF / LOCK EXC / HALF SIGNIFICANT
DS90 0932.1640 RT= 65:50 +EI LRP 06/26/86 15:27 SUB
TIC= 100168 100%= 18226 LP32 LAM 10 FR18
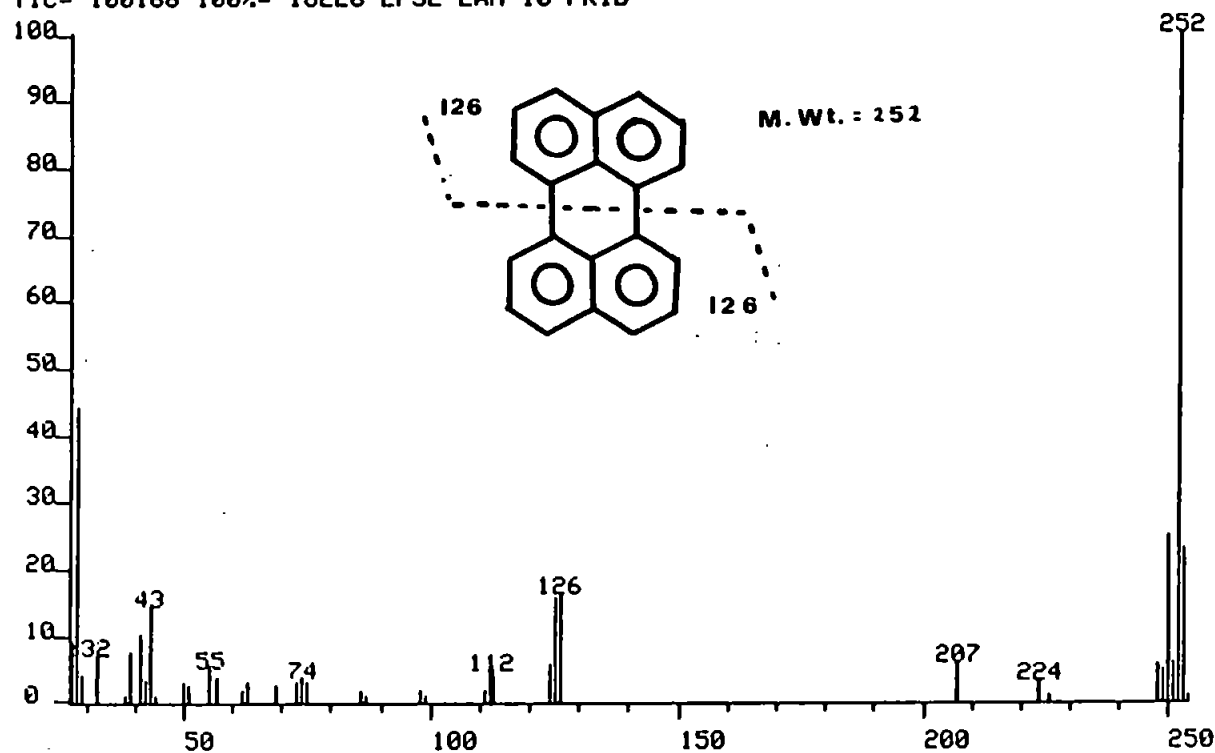
Figure 113. Mass Spectrum of the major aromatic peak from Core
L.P.32 lamination 10 identified as perylene (for
conditions see 4.4.8.3.).

Perylene in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
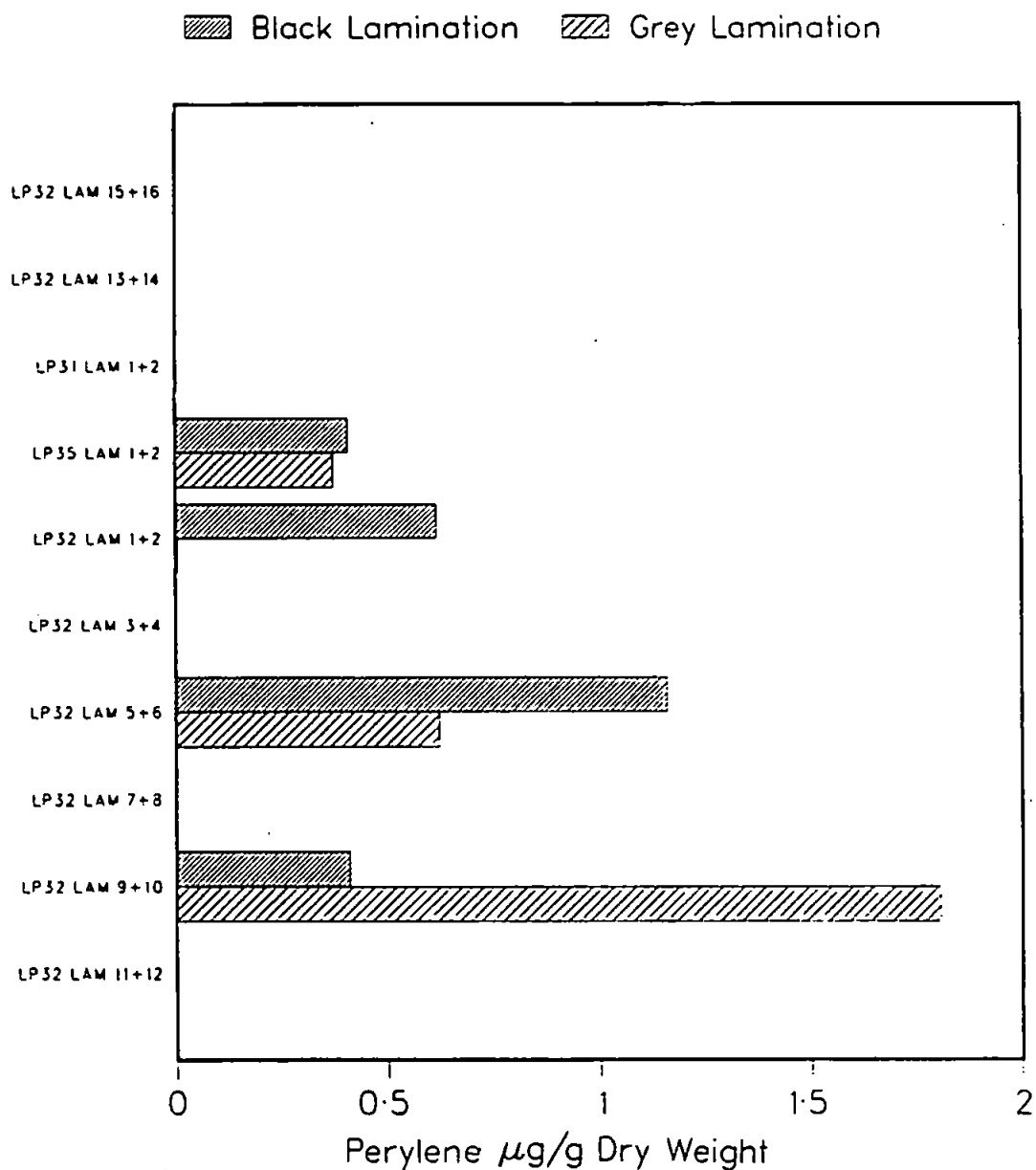
Figure 114. Distribution of Perylene in L.P.35 laminations 1 and 2, L.P.32 laminations 1,2,5,6,9 and 10 from Loe Pool.

Perylene in Loe Pool Sediment

▨ Black Lamination   ▨ Grey Lamination
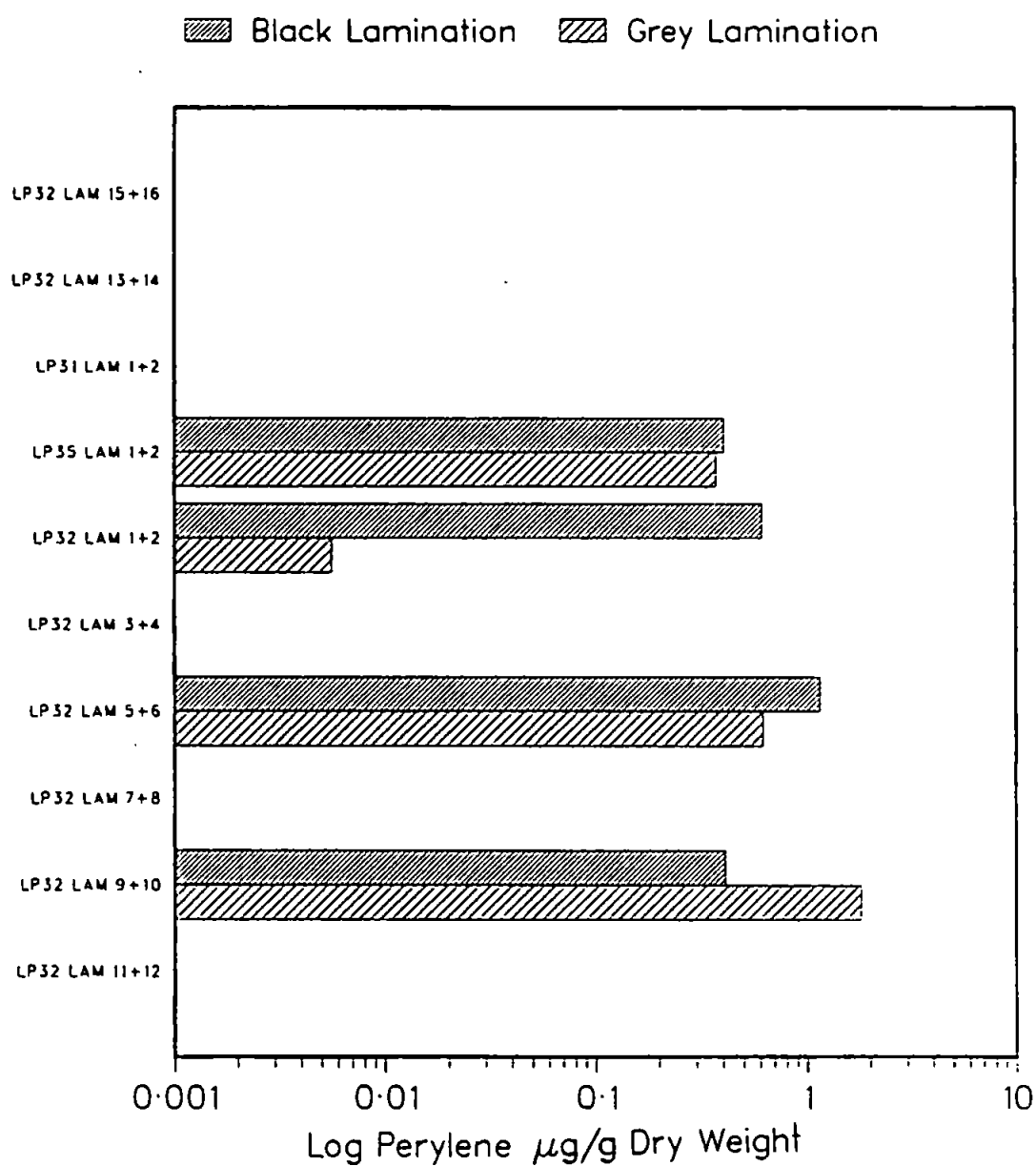
Figure 115. Distribution of Perylene (log scale) in L.P.35 laminations 1 and 2, L.P.32 laminations 1,2,5,6,9 and 10 from Loe Pool.

molecular ion (M) is at mass 328. The major ion at 313 is a M-methyl (M-15) fragmentation. The peak is identified as C 16 n-alkanoic acid according to the justification in Figure 118.

The chromatogram of L.P.35 lamination 2 (grey sediment) contains a homologous series of n-alkanoic acids with a range from C 10 to C 34 (Fig 116). The distribution is bimodal with a maximium at n-C 16 and a secondary peak around n-C 28. There is a very high even over odd predominance. In addition to the straight-chain acids many other compounds are present. These may include branched and cyclic saturated acids together with unsaturated and hydroxy acids.

The individual n-alkanoic acids C 12 to C 32 were quantified and are presented as a series of horizontal bar charts (Figs. 119 & 120). Odd numbered acids were not included because in most chromatograms they were only present in trace quantities. For this reason no C.P.I. could be calculated. The acid fraction from L.P.32 lamination 1 and 2 appeared to have degraded prior to analysis and therefore there are no results from this extraction. The bar charts (Figs. 119-120) have a similar trend to the chromatogram of L.P.32 lamination 2. Each extract from L.P. 35 and L.P. 32 had a bimodal distribution peaking at n-C 16 and n-C 28 alkanoic acids. In all extracts except L.P.32 lamination 10 the maximum mode was at n-C 16. The acid extract from L.P.31 only contained trace quantities of the secondary mode around n-C 28.

LP 32 lamination 2   acid fraction derivatised with B.S.T.F.A.
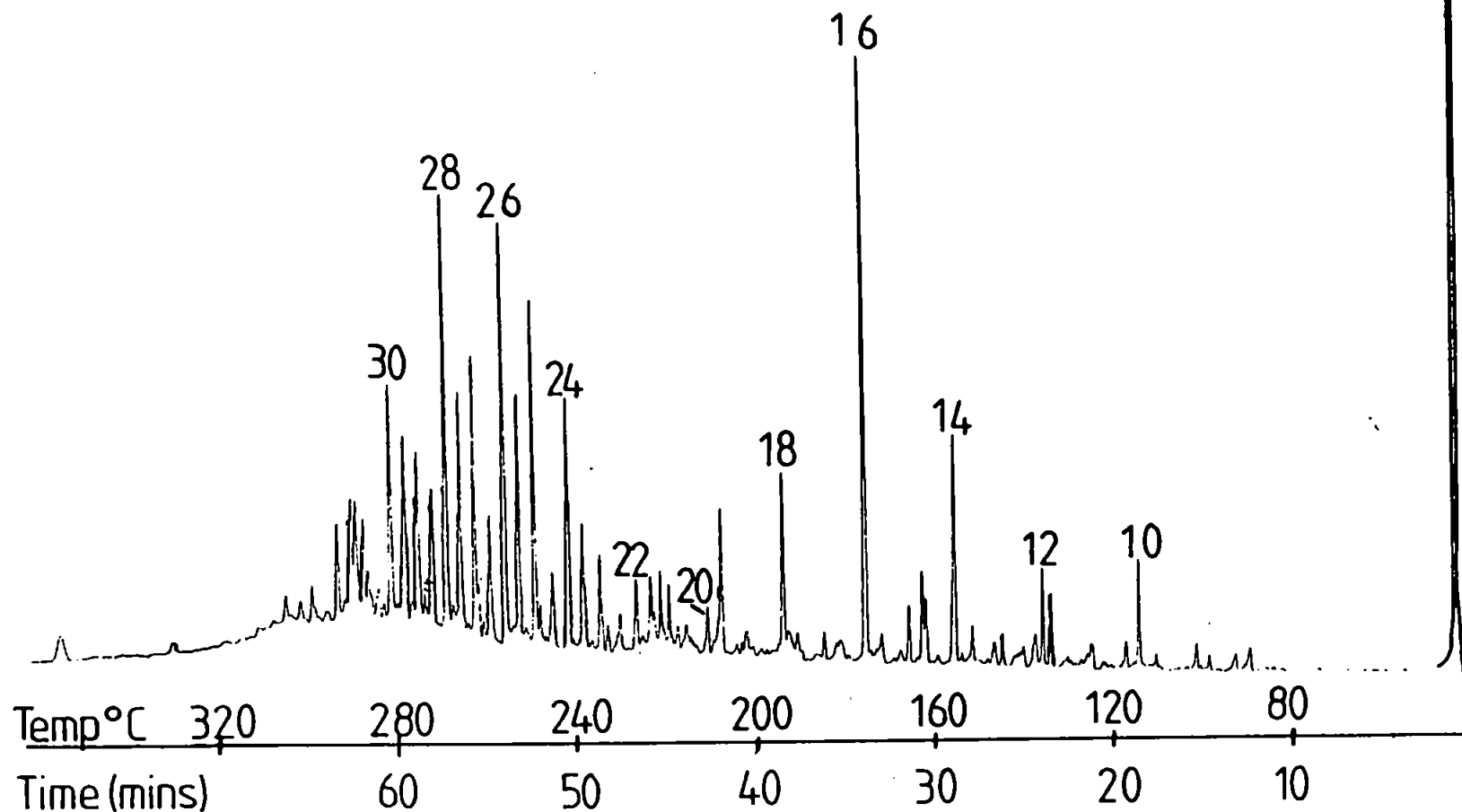
Figure 116. Chromatogram of T.M.Si Alkanoic Acids of L.P.32
lamination 2 from Loe Pool (for conditions see section
4.4.8.2.).
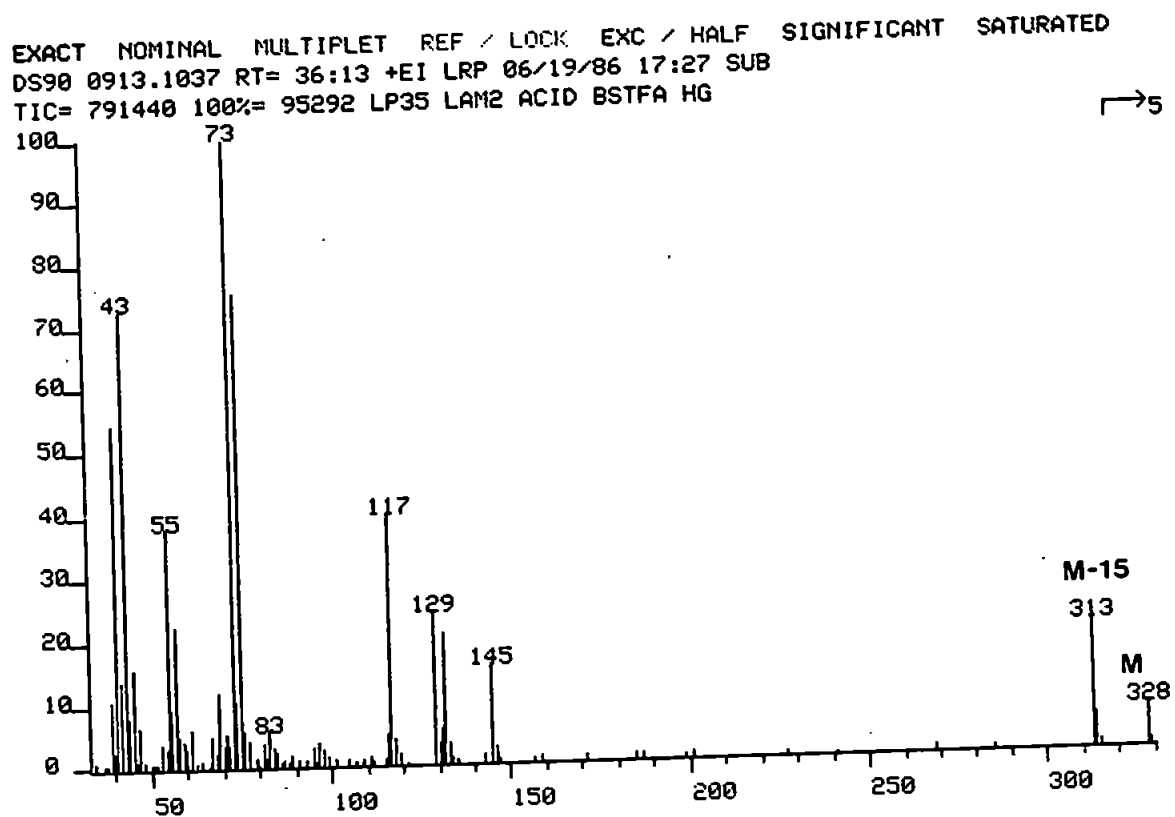
Figure 117. Mass Spectrum of n - C 16 T.M.Si Alkanoic Acid
(for conditions of analysis see section 4.4.8.3.).
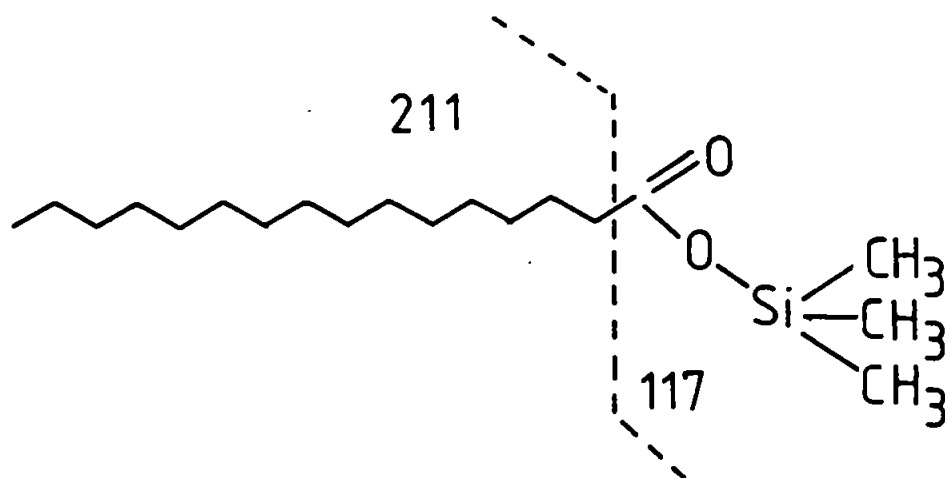
Figure 118. Structural formula of T.M.Si C 16 alkanoic acid
(Molecular weight = 328) showing fragmentation to
produce 117 ion.
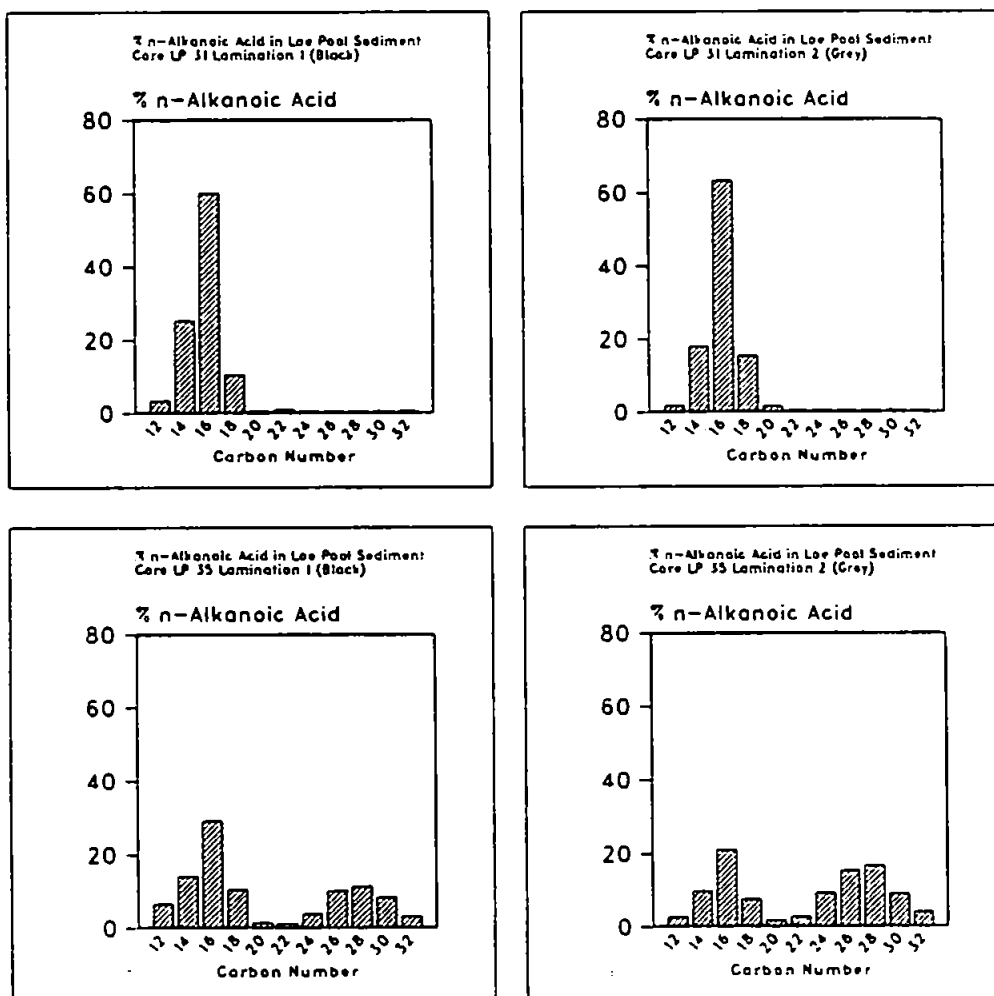
Figure 119. Distribution of Alkanoic Acids in L.P.31
and L.P.35 laminations 1 and 2 from Loe Pool.
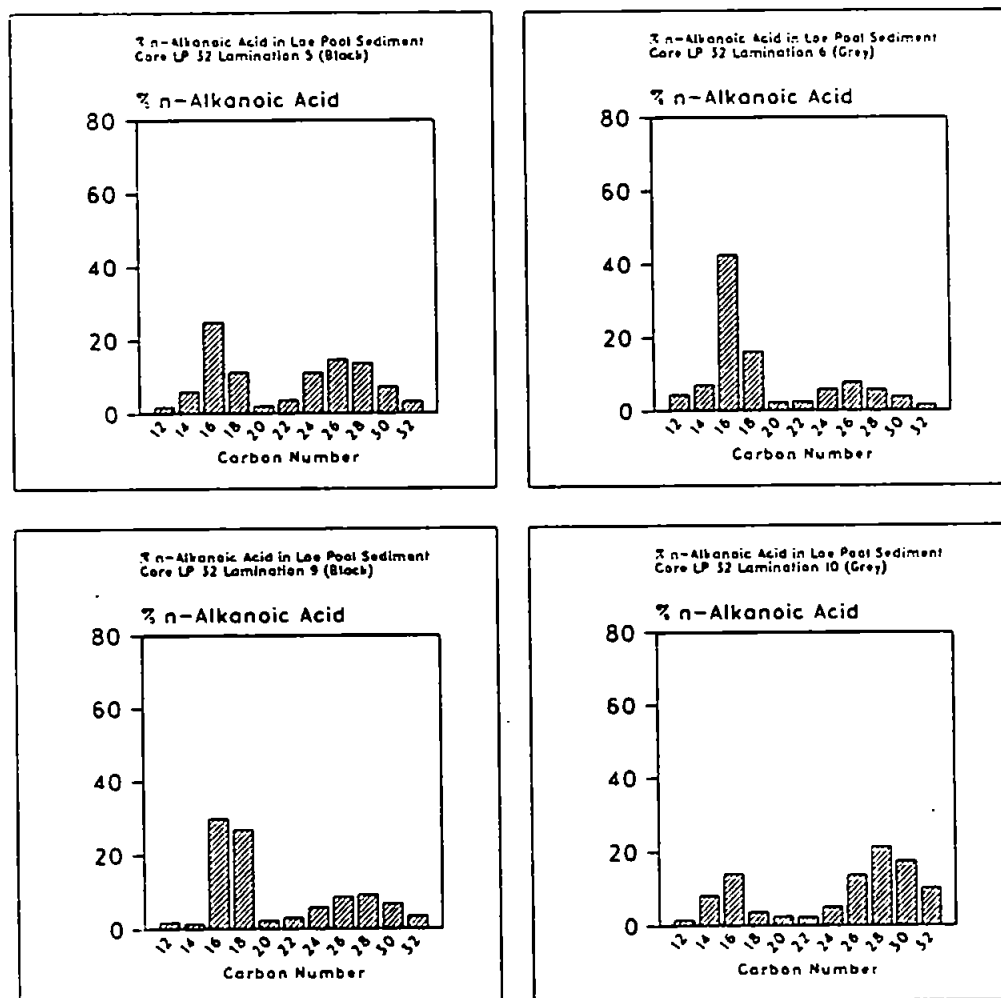
Figure 120. Distribution of Alkanoic Acids in L.P.32
laminations 5,6,9 and 10 from Loe Pool.

6.0 Discussion

6.1 Core Location

The sediment formed in Loe Pool was known to contain several different stratigraphic units (Simola et al., 1981). The depth of each of these varied across the lake bed. Choice of sampling location was influenced by the detail of each sediment stratigraphy and the ease with which the core could be retrieved. The top brown clay gyttja contained greatest detail at site H (Fig. 10, Plates 1 & 2). The regular black/grey laminated sediments were most easily obtained by "freezer corer" at site A. These laminations are known to exist below the brown and pink clays deposited at site H. However, the black/grey sediments were below 2m of sediment and so could not be readily retrieved using either the 1m mini-Mackereth or the freezer corers.

6.2 Core Stratigraphy

The sediment formed in Loe Pool contains five main stratigraphic units as described in section 2.3. The cores examined in this study included the following stratigraphic units (section 5.2):

1)   laminated brown clay gyttja

2)   red laminated clays

3)   massive grey clay

4)   black/grey annual laminations

The similarity of the sediment reported in this study with that from previous work illustrates the uniformity of the sediment deposition across the lake bed.

The dates assigned to the cores were based on previous analysis of sediment (Simola et al., 1981) and historical evidence (Coard, in prep.). This information is summarised in section 2.3. The brown clay gyttja (0-35cm depth for L.P.6) has approximately twenty discrete laminations. These cannot be annually-formed because this deposition would infer a sedimentation period of 10 years. This contradicts the 137-Cs data and historical evidence of mining activity which indicates that the brown clay gyttja has been formed since approximately 1940.

Beneath the brown clay gyttja are a series of pink and black laminated clays (35-53 cm for L.P.6). The major laminations are thought to have been produced annually (Simola et al., 1981). In addition, there are a number of microlaminations. Their period of formation has not been identified.

The massive grey clay layer (53-66cm for L.P.6) does not contain any regular laminations. This may be because either the layer represents one season of deposition, or the conditions causing the formation of laminations did not exist at this time. The black and grey varves present below the grey clay have been characterised as annually-forming by analysis of their diatom stratigraphy (Simola et al., 1981). In this study these black/grey varves were analysed for several physical and chemical variables. The results of this work are discussed in detail throughout this chapter.

6.3 Physical Characteristics of Loe Pool Sediment

6.3.1 Dry weight of Core L.P.6

The dry weight per gramme wet sediment in core L.P.6 is illustrated (Fig. 38). The increase in dry weight with depth down the core is probably caused by compression. The disturbance of this trend during the 1930's may be attributed to the sedimentation of mine waste. The material deposited in this period contained a high proportion of fine dense clays which increased the dry sediment.

6.3.2 Dry Weight of Cores L.P. 31, L.P. 32 and L.P. 35.

The increase in dry weight noted in most of the grey (winter) laminations (section 5.3.2, Fig. 39), may be caused by fluctuations in the type of dry matter deposited. During the winter, erosion is at a peak and so a higher proportion of minerogenic matter would be deposited. In contrast, during the summer erosion would be lower, but production and deposition of relatively less dense organic compounds will be at a maximum. These factors may account for the seasonal variations of dry weight in the black and grey laminations.

6.3.3 Loss on Ignition of Core L.P.6

The loss on ignition (L.O.I.) for core L.P.6 is shown in Figure 40. The results indicate that the L.O.I. has increased from the

1930's to the present day. The minimum values of approximately 5% L.O.I. per gramme dry weight correspond with the red/black sediment deposited in the period of intense mining from 1936 to 1940. The mine waste would have consisted of primarily inorganic debris. The low value of L.O.I. may not necessarily infer a reduction in quantity of organic matter deposited to the sediment, but instead a dilution by minerogenic material. Historical reports suggest that the River Cober and Loe Pool were tinged a red colour (Coard, in prep.). However, it would seem likely that this pollution would cause a reduction in the photic zone and also have possible toxic effects on aquatic organisms. These factors would decrease aquatic production and subsequently the deposition of organic matter to the sediment. The increase of L.O.I. in the sediment from 1940 to the present day is consistent with evidence of the eutrophication of the Pool (Simola et al., 1981; Coard et al., 1983). The apparent increase in L.O.I. from around 4-10% in 1930-1940 to 15-20% at present may be caused by a combination of increased production of organic matter by aquatic organisms and a decrease in the proportion of minerogenic matter.

There is no regular pattern of L.O.I. with sediment colour in the brown clay gyttja or the red/black laminated sediments (Fig. 40). The black or darker layers tend to have a higher L.O.I. than lighter layers, which suggests that the darker layers may have been deposited when organic input and/or sedimentation conditions allowed greater preservation of organic matter. This infers a summer period of deposition for the black layers. In this season productivity of organic matter is greatest and conditions are most conducive for anoxia. Such conditions aid the preservation of

organic matter.

The comparison of % L.O.I. of Loe Pool sediment with other lakes is shown in Table 25. Loe Pool has a lower L.O.I. range than published results of a selection of other lake sediments. This may reflect the past mining activity which has contributed a high inorganic sediment load to the lake. Although mining has now ceased there are areas of derelict mine works with unstable land liable to erosion. In addition, there has been an increase in the area of ploughed land from the 1940's (O'Sullivan pers. comm.), which also may have provided a source of minerogenic material.

Mackereth (1966) noted that L.O.I. is sometimes used as an estimate of organic matter. He suggested that where the sediment is composed of largely inorganic matter then serious errors in estimates of organic matter may occur. Results of % organic carbon (section 5.6) from the black/grey laminated sediments indicate organic carbon concentrations in the range 1-2%. Clearly, the levels of L.O.I. presented are caused by loss of some other material as well as organic matter. Mackereth (1966) suggested that this material is most likely to be water held within the mineral lattice even at temperatures of 110°C. The interpretation of the results of L.O.I. should, therefore, be treated with caution.

6.3.4 Loss on Ignition in Cores L.P. 31, L.P. 32 and L.P. 35

The L.O.I. for the individual black and grey laminations analysed from cores L.P.31, L.P.32 and L.P.35 are presented in Figure 41. The trend is for the black (summer) laminations to have a higher L.O.I. than the grey (winter) sediment (section 5.3.4). An

Lake Sediment	Loss on Ignition (%)	Reference
Loe Pool	0.05-0.25	This study
Shagawa Lake	20-30	Gorham and Sanger, 1976
Rudetjärn	10-30	Renberg, 1978
Lake of the Clouds	10-50	Anthony, 1977
Harvey's Lake	20-45	Engstrom et al., 1985
Alderfen Broad	60-95	Moss et al., 1979
Mirror Lake	2-40	Davis and Ford, 1982

Table 25. Comparison of Loss on Ignition values in Lake Sediment between Loe Pool and other Lacustrine sites.

explanation for this based on increased production of organic matter and better preservation following sedimentation has been outlined in section 6.3.3. If, as Mackereth (1966) suggested, the results of L.O.I. are caused to a large extent by water loss, then the results are not without value. If the black (summer) L.O.I. is elevated because of higher water content, then the actual variation in seasonal dry weight per gramme wet weight is even more significant than reported in section 6.3.2.

6.3.5 Combustion Residue in Core L.P.6

The combustion residue (C.R.) is illustrated for core L.P.6 in Figure 42. The profile is inversely proportional to that for the L.O.I. (Fig. 40). The C.R. is greatest in the lower half of the core which includes the sediment deposited during the period of most intense mining operations from 1930 to 1940. In contrast, the most recent sediment has been formed under increasingly eutrophic conditions and, therefore, the % minerogenic material is decreased. It should be emphasised that the differences between pre- and post 1940 C.R. values are small. This illustrates that the sediment is dominated by the deposition of inorganic matter in each of the stratigraphic units measured.

6.3.6 Combustion Residue in Cores L.P.31, L.P. 32 and L.P. 35

There is a trend of a slightly higher concentration of minerogenic matter in some of the grey (winter) than the black (summer) laminations (section 5.3.6, Fig. 43). This may be caused by a

higher proportion of minerogenic matter being deposited under
conditions of seasonally-high erosion rates in the winter.
However, these differences are small compared with the large
fluctuation in streamflow between seasons. From this it may be
inferred that minerogenic matter dominated input to the sediment
throughout the year, from the 1920's to the 1930's when these
laminations were deposited.

6.4 Magnetic Variables in Loe Pool Sediment

6.4.1 The Range of Magnetic Susceptibility, S ratio,

            S.I.R.M. and S.I.R.M./Susceptibility

The range of magnetic variables analysed from the Loe Pool
sediment are summarised as follows:

Magnetic variable	Units	Range in 3 cores from Loe Pool sediment
Susceptibility	$10-6$ G.Oe-1cm-3g-1	2-17
S.I.R.M.	$10-6$ G. cm-3 g-1	350-3500
S.I.R.M./χ		120-500

(section 5.4., Figs. 44-53).

By reference to Figure 14 it is seen that these results are
consistent with a high concentration of haematite. Additionally,
the range of magnetic variables analysed indicate a low
concentration of ferrimagnetic minerals. The S.I.R.M. and
S.I.R.M./susceptibility values are typical of the

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anti-ferromagnetic mineral, haematite.

It was noted (section 5.4) that there were differences in all magnetic variables both down each sediment profile and between cores from different sites. According to Dearing et al. (1981) "the major susceptibility fluctuations in sediment cores are usually caused by changes in either particle size of the minerogenic component of the sediment or by changes in the magnetic mineralogy of the eroded sediment" (p.359). In core Ml, the magnetic susceptibility exhibits the greatest change in the laminated red/black and grey clays (Fig. 45). These were deposited in the period 1930-1940 when very intense mining occurred in the catchment area. The variations in susceptibility are likely to be caused by either one or a combination of the reasons proposed by Dearing et al.(1981).

The brown clay gyttja deposited post 1940 has a magnetic susceptibility of 7 ± 1 in cores L.P.6 and Ml (Figs. 44 & 45). These are higher values than for sediment deposited pre-1930. This suggests that the pre-1930 sediment contains lower concentrations of ferrimagnetic and anti-ferromagnetic minerals than that sediment deposited post 1940. Possible reasons for this are 1) dilution of pre-1930 sediment by mine waste with a relatively low concentration of magnetic minerals and 2) greater input of ferrimagnetic material to the brown clay gyttja from an increase in soil erosion caused by ploughing.

The S.I.R.M. and S.I.R.M./susceptibility have highest values in the red/black laminated sediments in cores Ml and L.P.6 (Figs. 48-52). This infers that the relative concentration of anti-ferromagnetic minerals, such as haematite, were greatest

during the sedimentation of this material. The result is consistent with visual evidence from the core and with the known history of mining within the catchment. It may be concluded that the S.I.R.M. and S.I.R.M./susceptibility values were greater during this period of high sedimentation because of the increased supply of haematite from mining activity.

6.4.2 Correlation of Magnetic Variables between Cores

It was reported in section 5.4.5 that there were visual similarities in the profiles of magnetic susceptibility analysed from cores L.P.6 and M1 (Fig. 54). The apparent correlation between the same stratigraphic units of sediment from cores collected approximately 200 m apart from sites A and H (Fig. 10), illustrates the uniformity of material deposited across the lake bed at any one time in the lake's history. In addition, the profiles indicate that once deposited the sediment is not liable to extensive mixing caused either by physical disturbance or bioturbation.

The profiles also illustrate that there is a higher average susceptibility in core M1 than in core L.P.6. This difference may be caused by differential deposition across the lake bed. Core L.P.6 was collected from site H (Fig. 10). This is within an apparent area of deltaic deposition from the River Cober (O'Sullivan et al., 1982). Core M1 originated from an area some 200-300m further away from the inflow of the River Cober, in a location where sedimentation is less rapid (Fig. 10). Sediment deposited at site H (for example L.P.6) would, therefore, contain a higher proportion of mine waste than material at site A (for

example M1). It follows that the sediment deposited at site H is likely to contain a higher proportion of coarser minerals than sediment at site A. Magnetic susceptibility is partly a function of grain size (Thompson et al., 1975). As a consequence the smaller and denser particles deposited at site A may have a greater susceptibility than minerals at site H.

6.4.3 Correlation of Different Magnetic Variables from the
Same Core

The correlation between S.I.R.M. and magnetic susceptibility is presented in Table 14. There is a linear correlation of +0.79 and + 0.809 for the whole cores L.P.6 and M1 respectively and +0.28 for the brown clay gyttja and +0.92 for the laminated red/black and grey clay from L.P.6. Thompson (1979) reported that in a suite of samples in which a single type of magnetic mineral is dominant or in which the magnetic minerals occur throughout in constant proportion, there will be a direct linear relationship between susceptibility and S.I.R.M. During the 1930's the mines supplied the greatest proportion of magnetic minerals to the sediment. Consequently, the red/black and grey sediment had a particularly high linear correlation. There is no correlation in the brown clay gyttja which indicates that the magnetic assemblage is more mixed. This is probably because of the decreased proportion of mine waste as a major sediment source.

The correlations calculated illustrate the significance of mine material in the accumulation of sediment in Loe Pool.

6.4.4 Magnetic Variables in Core L.P. 32

There are no apparent differences in the measurements of magnetic susceptibility, S ratio, S.I.R.M. and S.I.R.M./susceptibility from the seasonally-deposited sediment from core L.P.32 (Figs. 46, 47, 50 & 53). This is probably because mine waste dominated the input of magnetic minerals during the period when these laminations were deposited. If it is assumed that the mines were operational throughout the year the concentration of magnetic variables would not show any seasonal differences. With a constant proportion of magnetic minerals being sedimented there would not be any differences of magnetic variables despite changes in the volume of matter being eroded between the summer and winter seasons.

6.5 Metals in Loe Pool Sediment

The analysis of elements in lake sediments has many applications in palaeolimnology (section 3.4). This section will discuss the results of metals analysed presented in chapter 5 with reference to this introduction.

6.5.1 Iron and Manganese

The ranges of the iron (Fe) and manganese (Mn) concentrations in Loe Pool sediment are below the crustal average and in the lower half of the distribution at many lacustrine sites (Table 15). There are two important factors which differentiate Loe Pool from many of

the other lakes quoted:

1) The black/grey laminations analysed were deposited under conditions of high rates of erosion from the catchment. O'Sullivan et al., (1982) calculated that the erosion rate was approximately 174 tonnes Km-2 year-1 (Table 3), with a subsequent sediment accumulation rate of 3 cm year-1 (Simola et al., 1981).

2) The analysis performed in this study was based on a "partial" 0.5M HCl extract. Some of the results in Table 15 were from "total" extracts. Such "total extraction techniques would be expected to liberate a larger quantity of elements from the sample under investigation than "partial" extracts.

Therefore, a smaller concentration relative to other studies is reported (Table 15). This is because of a) dilution by a large quantity of minerogenic matter and b) the authigenic fraction only is analysed.

It is interesting to note from Figure 55 that there is a higher concentration of authigenic iron in eight of the black than the grey laminations. A possible reason for this relationship is seasonality of rainfall and streamflow. The River Cober is known to have over 3 times as much water flowing into Loe Pool in the 6 months from November to April than the rest of the year (section 2.1.4). The consequential erosive power of the Cober during the winter season would be higher than in the summer, so producing a seasonal bias in transport of minerogenic matter. If, as already discussed in this section the mining waste has a low concentration of readily extractable iron, then the effect of the winter sedimentation would be to dilute authigenic iron from other

sources. This may explain why the concentration of iron presented in this study is higher in the black (summer) than the grey (winter) laminations.

The concentration of manganese in Loe Pool sediment (Fig. 56), is also subject to dilution by minerogenic matter. However, there is a greater concentration of manganese in eight of the grey (winter) than black (summer) layers. Either there is a higher proportion of extractable manganese in the mineral matter or some factor is limiting the deposition of this element in the black (summer) sediment. Manganese is known to change from the insoluble Mn^{4+} oxidised state to the readily soluble Mn^{2+} if conditions become reducing. Evidence from Loe Pool already suggests that in the summer months there may be periods of oxygen stress at the sediment-water interface (section 2.2.2). Such anoxia was probably more prolonged in the past when the lake was relatively deeper. The behaviour of manganese in the Loe Pool sediment is similar to that of the seasonally-anoxic Esthwaite Water (Fig. 17, section 3.4.2 and Fig. 56). Mackereth suggested that the lower concentrations of manganese in Esthwaite Water were caused by reducing conditions at the sediment-water interface (section 3.4.2). It seems possible that the reason for the distribution of manganese in the seasonal laminations at Loe Pool is the dissolution of the element from the sediment deposited in the summer by the reducing conditions and the reprecipitation at overturn when the manganese is oxidised to the 4+ state.

This hypothesis can be examined by reference to the Fe:Mn ratio (Fig. 57). The ratio is considerably greater in the black (summer) than the grey (winter) laminations. This is additional evidence of

an anoxic hypolimnion during the summer months. Under reducing conditions manganese would be more readily solubilised than iron so increasing the Fe:Mn ratio in the surface sediment. At overturn, when the bottom waters are reoxygenated the manganese in solution would be oxidised to the +4 state and reprecipitated to the sediment. This would lower the Fe:Mn ratio throughout the winter months.

The range of the Fe:Mn ratio at Loe Pool matches most closely that of Esthwaite Water (Table 16). Mackereth (1966) concluded that the most important factor governing the fluctuations of the Fe:Mn ratio in Esthwaite sediment was the lake basin redox condition. In Esthwaite Water the Fe:Mn ratio has been used to record the palaeo-redox conditions over a time span of thousands of years. Calculation of the Fe:Mn ratio for the seasonally-deposited black/grey laminations may also identify palaeo-redox conditions. However, changes can be plotted over an annual time scale. From the results of the Fe:Mn ratio it may be concluded that the black (summer) laminations were formed under reducing conditions and the grey (winter) sediment deposited when the lake water was oxygenated.

The sediment was not examined for individual iron or manganese species. However, it is interesting to speculate whether the colouration of the sediment deposited in the summer is caused by the formation of black metallic sulphides under anoxic conditions. It should be noted that such sulphides may not have formed directly from the reducing conditions. They could develop following deposition, as the decay of organic matter utilizes all available oxygen and reduces metallic oxides or hydroxides to sulphides.

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6.5.2 Sodium, Potassium, Magnesium and Calcium

The concentration of the elements sodium (Na), potassium (K) and magnesium (Mg) in the laminated sediments formed in Loe Pool are in the bottom half of the typical lacustrine sediment elemental concentrations (Table 15). As suggested in section 6.5 low concentrations of elements reported from Loe Pool may be a function of the "partial" extraction technique used. The alkali and alkaline earth elements generally form approximately 2% of the Earth's crust (Table 15). A high proportion of these elements are often locked up in a mineral lattice and can only be quantified following "total" extraction.

Calcium is more readily leached from mineral matter than sodium, potassium, and magnesium. This may explain the relatively higher concentration of calcium present in some of the black/grey laminations than in other lacustrine sediments (Table 15). The levels of calcium may also reflect the presence of carbonates and limestone within the catchment (section 2.1.1).

It may have been expected that sodium and potassium had a seasonal bias, with a greater concentration in the winter than the summer layers. This is because elevated levels of alkali metals have been correlated with increased erosion rates (Mackereth, 1966). However, there is no apparent seasonal bias in potassium (Fig. 59), and there is a higher concentration of sodium in the black (summer) rather than the grey (winter) layers (Fig. 58). The conclusions

reached by Mackereth were based on a "total" extract. The Loe Pool sediment was only subjected to a "partial" hot 0.5M HCl dissolution. This would not liberate sedimentary sodium and potassium in a mineral matrix. Analysis of the combustion residue in Loe Pool sediment (section 5.3.6.) revealed that the concentration of minerogenic matter was similar throughout the year. It may, therefore, be expected that the concentrations of sodium and potassium in the sediment would also be similar throughout the year. This explanation holds true for potassium, but cannot explain why sodium does not follow a similar trend. Possibly there are factors other than erosion that are important in the accumulation of authigenic sodium.

The alkaline earth element, calcium, has a strong seasonal bias, with significantly higher concentrations in the grey (winter) than the black (summer) laminations (Fig. 60). Mackereth (1966) suggested that elevated concentrations of calcium only occurred when erosion in the catchment was so intense as to prevent removal first by leaching. If this theory is applied to the levels of calcium in Loe Pool sediment it may be concluded that the high winter levels are produced by very intense erosion. However, although there would be a greater quantity of calcium deposited in the grey (winter) than the black (summer) laminations, the actual concentration should remain the same. This is because intense erosion would also lead to a proportional increase in the volume of other minerals. If the distribution of calcium in the Loe Pool sediment cannot be explained by changes in input then it may be inferred that there is another mechanism moderating the deposition of calcium to the lake sediment.

Possible processes include association with organic matter and dissolution under seasonally-reducing conditions. Mackereth (1966) found an association between calcium and organic matter. However, there is no strong variation in the concentration of organic matter to support such a link (Fig. 69). The second possible reason for the rhythmic variation in sedimentary calcium concentration is the influence of sedimentary redox conditions. The distribution of calcium in the laminated sediment may be explained, as follows. In the winter season calcium enters the lake and is readily precipitated to the sediment. In summer the calcium entering the lake would also be precipitated with the remainder of the mineral load. If the minerals fall through the oxygenated surface to a reduced bottom waters, then the calcium which is readily leached in reducing conditions would be redissolved. In addition, calcium present on the sediment surface would also be subject to dissolution. This would reduce the concentration of calcium deposited under reducing conditions. At overturn, bottom waters would be reoxygenated so allowing rapid precipitation of the calcium held in solution. Hence, the concentrations of calcium in the black and grey laminations may indicate seasonal anoxia in the bottom waters during the summer months.

6.5.3 Lead, Zinc, Cobalt, Copper and Nickel

The concentrations of lead (Pb), zinc (Zn), cobalt (Co) and copper (Cu) are greater in the black and grey laminations from Loe Pool than in a selection of other lacustrine sediments (Table 15). As only a "partial" extraction technique was used for the results

presented in this work, the concentration of heavy metals analysed is probably even greater in Loe Pool than the other lacustrine sediments.

The black and grey laminated sediments were formed at a time of extensive mining within the catchment. Residue analysed from some mine tailings in Cornwall have been reported to contain very high concentrations of heavy metals (Yim, 1981). The high concentrations of heavy metals reported from Loe Pool (section 5.5.5) are a further indication of the large quantity of mine waste deposited in the lake.

The concentration of the elements Copper, Zinc and Cobalt all have a seasonal bias, with highest concentrations present in the black (summer) laminations. Of these, statistically strongest variations are found with copper (section 5.5.5). There are several possible reasons for this.

Hamilton-Taylor et al. (1981) have suggested that in lakes with an anoxic hypolimnion some form of copper cycling occurs with a similar pattern to manganese. However, such a mechanism if it occurred in Loe Pool would produce a winter maximum of copper.

Rowlatt (1980) proposed that copper has a strong transport association with organic matter. A further factor affecting copper is that the element is geochemically mobile. The element may be both leached and eroded from the catchment. At Loe Pool, erosion would be the dominant source of copper in the winter months. However in the summer months erosion would be reduced because of the reduction of streamflow and so leaching as a source of copper to the lake may become proportionally more important. This would result in a larger quantity of copper relative to other minerals

entering the Loe Pool system in the summer.

It is difficult to assess from the data available which of these processes, if any, may be responsible for the increased concentration of copper in the black (summer) laminations. Interpretation of these results based on theories established at other sites must be treated with caution because of the high pollution load of copper.

It was noted in section 5.5.5 that with the Co:Ni ratio seven of the varves had a higher ratio in the black than grey layers (Fig. 68). It is interesting to note from Mackereth (1966) that he observed a striking relationship between the concentration profiles of iron and manganese and those of cobalt and nickel. No such clear relationship is discernable at Loe Pool, although there is similarity between the Co:Ni ratio and Fe:Mn ratio. This suggests a sedimentary relationship between the elements iron and cobalt and between manganese and nickel, which is consistent under both winter (oxidising) and summer (reducing) conditions.

6.6 Organic Carbon and Nitrogen

The range of % carbon and % nitrogen in the black and grey laminated sediments formed in Loe Pool is very low in comparison with other lacustrine sediments (Table 17). This may be caused by one or a combination of the following factors:

1) Very low productivity in the lake system

2) Sedimentation of material with a low organic content.

Historical evidence of mining activity and analysis of other

chemical and physical variables indicates that there was a very high input of minerogenic matter from mining activity during the 1920's and 1930's. The mine waste would dilute any organic carbon and nitrogen deposited. In addition, aquatic productivity may have been reduced by toxic effects of the increased heavy metal load.

The low concentrations of both organic carbon and nitrogen reported in section 5.6 are consistent with this reasoning. It may be concluded that the % organic carbon and % nitrogen are low because of the influx of highly minerogenic mine waste.

The analysis of organic carbon in the black (summer) and grey (winter) laminations (Fig. 69) did not reveal any differences with season of deposition. It may have been expected that there would be a higher proportion of organic matter in the black (summer) laminations when production would have been higher and lake oxygen levels lower, so allowing better preservation. It may be concluded that at this period the additional autochthonous input of organic carbon in the summer months is insignificant in comparison with the allochthonous contribution throughout the year.

The organic carbon:nitrogen (C:N) ratio does show a range similar to those found in other sediments (Table 17). This suggests that the concentration of both carbon and nitrogen has been reduced equally in comparison with other lake sediments. This is consistent with the conclusion that the low levels of organic carbon and nitrogen in the Loe Pool sediment are caused by a sediment input dominated by highly minerogenic matter.

It was noted in the results section that the concentration of nitrogen is higher in eight of the black (summer) than grey (winter) laminations and that the C:N ratio was higher in the grey

lamination in eight out of the ten varves analysed (Figs. 70 & 71).
Care must be taken in reaching conclusions from this data as there
is no statistical evidence to support the trend. However, the
results agree with the hypothesis put forward in section 3.5. Here
it was indicated that allochthonous organic debris tended to be
depleted in compounds containing nitrogen and enriched in those
consisting largely of carbon. Hence, the C:N ratio of material with
a mainly terrestrial origin would be relatively high. In contrast,
the C:N ratio of marine plankton, which may be representative of
autochthonous production, was much lower.

At Loe Pool the input of terrestrial organic matter would
maximise in the winter with increased erosion and the aquatic
production peaks in the summer, so the C:N ratio may be expected to
show a seasonal variation. The average black (summer) C:N ratio is
10.7 compared with 12.8 in the winter (section 5.6). The difference
is not great, possibly because of the input of allochthonous
organic matter throughout the year. However, the results are
consistent with the hypothesis put forward in section 3.5. That is,
that, in annually-laminated sediment it is possible to distinguish
between the proportion of allochthonous and autochthonous organic
material by the C:N ratio. At Loe Pool the black sediment was
associated with higher autochthonous production and the grey with a
greater proportion of terrestrial organic matter.

6.7 Humic Acids in the Black and Grey Laminated Sediment

In the introduction to humic substances (section 3.6), results

from other lacustrine sites were outlined. The concentration of humic acids was reported to be greater in sediment formed under anoxic than the oxic bottom waters. The results presented in this study (Table 18 & section 5.7) show that the concentration of humic acids in the two varves analysed from Loe Pool are greater in the black than grey laminations. Evidence from the literature (section 3.6) indicates that higher concentrations of humic acids may be expected in reducing than oxidising conditions. The results from Loe Pool indicate that there is a greater concentration of humic acids in each of the summer than the corresponding winter laminations. This is further evidence that the bottom waters were anoxic during the summer season when the black sediment was deposited. Additionally, the summer is the time of greatest production, so conditions are optimum for the production, deposition and preservation of humic acids.

A further factor which may influence the concentration of humic acids is the quantity of other material being deposited. It is possible that because the input of clastic material peaks in the winter months, the lower concentration of humic acids in the grey (winter) sediment may be caused by dilution with minerogenic matter.

It may be concluded that the concentrations of humic acids in the black and grey laminations are consistent with the bottom waters of Loe Pool being anoxic in the summer and oxic in the winter months.

6.8 Carbonate in the Black and Grey Laminated Sediment

Carbonate may be formed in lake sediments as a result of four processes. These were discussed in section 3.7 and are summarised from work by Kelts and Hsū (1978):

1) Input from the erosion and transport of allochthonous carbonates.

2) Production of calcareous skeletons, structural parts and internal waste products within living organisms.

3) Primary inorganic precipitation and sedimentation of carbonate minerals.

4) Post depositional changes or early diagenetic reactions.

At Loe Pool it is possible that the carbonates may have formed from one, or, a combination of these processes. There is a source of carbonates and limestone within the catchment (section 2.1.1) and organisms with calcareous skeletons are known to live in the lake (Coard pers. comm.). The third and fourth processes may also occur although there is no evidence to support this possibility.

The range of % carbonate in the black and grey laminated sediments formed in Loe Pool (section 5.8 & Fig. 72) is low compared with other lacustrine sediments (Table 19). This may be a consequence of a) low deposition of carbonate to the sediment and b) dilution of sedimentary carbonate by mine waste.

What is particularly distinctive about the % carbonate in Loe Pool sediment is the significantly higher concentration in the grey (winter) than black (summer) lamination (Fig. 72). This trend is

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similar to that described by Hilton and Gibbs (1984). They reported higher carbonate levels in the surface sediment of Esthwaite water in January than August. The authors suggested that this might be caused by increased rainfall and a subsequent increase in the supply of eroded material from the catchment.

Variations of carbonate content have also been found in lacustrine sediment. Peglar et al. (1984) reported a series of varves containing dark and light couplets. This work was outlined in section 3.7. The light laminations were found to be rich in carbonate. The authors concluded that the pale layers were deposited in late spring and early summer and the dark iron rich layers in the late summer, autumn and winter. Peglar et al. (1984) suggested that either photosynthetic removal of carbon dioxide or increased water temperature might cause the deposition of calcite. However, from contemporary limnological evidence the authors could not propose either of these mechanisms as being likely. It is important to note that Diss Mere is a hard water lake and that Loe Pool is a soft water lake. Accepting this difference, the identification of the black lamination as being deposited in the winter and the light coloured layer in the summer in the Diss Mere sediment, is in complete contrast to evidence from Loe Pool. In the laminated sediment formed in Loe Pool skeletal diatom evidence indicates that the black layer is produced in the summer and the grey layer in the winter season.

Peglar et al. (1984) suggested two mechanisms by which carbonate deposition may occur during the summer months in freshwater lakes. The results from Loe Pool (Fig. 72) indicate that there is at least one other mechanism, which is consistent with

carbonate deposition in the winter months. A mechanism by which greater concentrations of carbonate are deposited in the winter than summer months will now be explained, with regard to Loe Pool.

It is likely that carbonate is transported from the catchment to the lake throughout the year. In the winter months this carbonate will precipitate to the sediment and be rapidly buried. In the summer months carbonate would continue to enter the lake and, in addition, may be produced as a consequence of biological activity. However, in the summer months anoxia is thought to have developed in the bottom waters of the Pool (O'Sullivan et al., 1984). This conjecture has been further supported in this study by evidence from the Fe:Mn ratio. In reducing waters carbonate would be redissolved according to the equilibrium which is illustrated in Figure 20. This is in agreement with the conclusions reached by Degans and Stoffers (1976) concerning the deposition of calcite through periodically reducing waters. Therefore, calcite is not precipitated to the sediment in the summer months at Loe Pool because of the anoxic bottom waters. As a result the lake would become increasingly saturated with carbonate. At overturn (at the start of the winter season) the whole lake would be reoxygenated and there would be a sudden precipitation of carbonate to the sediment.

Throughout the remainder of the winter months calcite would then precipitate to the sediment in proportion to the rate of inflow to the lake. This assumes that the rate of deposition to the sediment is faster than dissolution as suggested by Rea et al. (1980) and outlined in section 3.7.

Accepting this proposed mechanism for the distribution of

carbonate in the seasonally-laminated sediment at Loe Pool, it may be concluded that the redox conditions in the bottom waters were the major influencing factor governing the deposition of carbonate to the sediment. This is in contrast to the conclusions reached by Peglar et al. (1984).

This conclusion reached from the laminated sediment at Loe Pool may not be applicable to a hard water body such as Diss Mere. However, if the redox conditions at the sediment-water interface were also the dominant factor at Diss Mere, then there appears to be two additional mechanisms for the formation of the black/white couplets at that site:

1) The white carbonate rich band formed after overturn following summer anoxia

2) The carbonate layer formed after overturn in the spring (assuming that the lake was frozen with reducing conditions overwinter).

It may be concluded that the analysis of sedimentary carbonate may be used to distinguish palaeo-redox conditions. From the concentration of carbonate in Loe Pool it is indicated that the black sediment formed under reduced bottom waters. Such conditions are consistent with the deposition of the black sediment in the summer months. In addition, the greater concentration of sedimentary carbonate in the grey layer is likely to have formed under oxic waters. This is consistent with the other evidence that the grey sediment was deposited in the winter months.

6.9 Pigments present in Loe Pool Sediment

It is difficult to compare actual concentrations of pigments present in Loe Pool sediment with other lacustrine sites. This is because different extraction and analytical procedures cannot be quantitatively compared. Jacobson (1978) noted that the spectrophotometric method may produce overestimates of up to 400%. There appears to be 10 times the quantity of chlorophyll a in the grey clay (Fig. 73) than in the black/grey laminated sediment (Fig. 77). It may be assumed that the grey clay should not have a higher concentration of chlorophylls than the black/grey laminations because both sediments were deposited under similar trophic conditions and at a period of intense mining. Pigments in the grey sediment were detected by a spectrophotometer (section 4.4.7.1) and in the grey clay by absorbance and fluorescence instruments following separation by H.P.L.C. (section 4.4.7.2). It seems likely that the core L.P.6 which was analysed by the spectrophotometric method has an overestimate of the concentration of chlorophylls.

The results for Core L.P.6 are not without value. Errors would be consistent for the same technique, so pigment concentrations may be compared down the core. In addition, it is possible to compare the trends indicated in the Loe Pool sediment with those from other lakes.

6.9.1 Chlorophylls a, b and c in Core L.P. 6

The barcharts of chlorophylls a, b and c (Figs. 73-75) indicate a sharp rise in pigment concentration in Loe Pool from the 1930's to the present day. There are at least three possible interpretations of this trend. These are based on a) the influence of mine waste, b) the eutrophication of the lake and c) the degradation of pigments with time.

Mine waste is known to have tinted the lake a pinky colour during the 1930's (Coard, in prep.). This visual pollution would almost certainly have reduced the photic zone in the lake. In addition some of the accompanying heavy metals in Loe Pool may have had toxic effects on the aquatic organisms. Both of these factors would reduce the level of aquatic production and hence the input of autochthonous pigment. Those pigments which were subsequently sedimented are likely to have exhibited a particularly low concentration because of dilution by the rapid accumulation of minerogenic matter throughout this period.

A second possibility is that the increase of the pigment concentration in the brown clay gyttja may have been caused by the eutrophication of the lake. The development of regular algal blooms (section 2.2) and analysis of the sedimentary properties of diatoms and phosphorus (section 2.3) have indicated an increase in the trophic level of Loe Pool. This increase in production may thus be reflected in the quantity of pigments deposited in the sediment.

Finally, the lower concentration of pigments in the black/red and grey clays may be caused by degradation of pigments with time. Pigments are known to be labile molecules. Even assuming a constant

input of sedimentary pigments a profile of a core would show increased degradation at greater sediment depths.

It is possible that all three mechanisms have had some influence on the sedimentary pigment concentration. The profiles of chlorophylls a, b and c (Figs. 73-75) are consistent with the input of high minerogenic loads in the 1930's and eutrophication of the lake from 1940 to the present day.

From Table 20 which illustrates the range of chlorophylls a number of points are apparent. First, the grey clay has a very uniform range of chlorophyll pigments. This suggests that the grey clay was deposited during a time when the input of pigments to the sediment was both low and stable. Such conditions would perhaps occur in one season, probably winter. If some of the clay had been deposited over a longer period of time, then the pigment concentrations would probably have shown greater variations. The actual concentrations of chlorophylls are low, a fact which is consistent with deposition during a non-productive season.

Variation in chlorophyll concentration is found in the black/red laminated clays (Figs. 73-75). In this stratigraphic unit each chlorophyll exhibits a wide range of values, the highest of which corresponds with a black lamination. Data from the Fe:Mn ratio (Fig. 57), diatom stratigraphy (Simola et al., 1981) and carbonate concentration (Fig. 72) of the black/grey sediment unit indicate that the black laminations were formed under anoxic conditions in the summer season. The high pigment concentration in the black rather than red layers in L.P.6 is also consistent with deposition in the summer season under anoxic conditions. This is because pigment production peaks in the summer months and that the

presence of seasonal anoxic conditions would enhance pigment preservation. The high concentration of chlorophylls a, b and c in this black lamination may indicate deposition during a summer season under anoxic conditions. The variation in chlorophyll concentration is the result of changes of productivity with season. Therefore, it is possible that the variation in the concentration of pigment may be used as a marker of seasonality.

The brown clay gyttja also exhibits variations of pigment concentration with lamination colour (Figs. 35 & 73-75, Plate 1). There is a tendency for the darker coloured laminations to have higher concentrations of sedimentary pigments. However this is not consistent for all laminations.

Core L.P.6 was collected at site H (Fig. 10) from a depth of approximately 2.5m of water. This is probably too shallow for prolonged anoxia in most summer seasons. The darker sediment would only be produced in anoxic waters formed under very stable lake conditions. Where the bottom waters were not anoxic then sedimentary pigments may accumulate in light brown sediment during a summer season. This reasoning may explain why there is no strong relationship between sedimentary pigment concentration and lamination colour.

The average concentrations of chlorophylls a, b and c in each of the stratigraphic units of L.P.6 have an interesting distribution (Table 21). In the black/red and grey clays there is a greater concentration of chlorophyll b than c. In contrast, there is more chlorophyll c than b in the brown clay gyttja layer. Chlorophyll c occurs mainly in algae and chlorophyll b in chlorophytes and terrestrial plants. Therefore,

it may be inferred that pigments in the black/red and grey clays have a strongly terrestrial influence and in the brown clay gyttja a relatively greater aquatic source. This conclusion supports the notion that the deeper grey and black/red sedimentary units were produced during periods of intense erosion. Further, the increased proportion of aquatically derived pigments in the brown clay gyttja is compatible with the increase in trophic status of the Pool since 1940. However, care must be taken with these conclusions because they are based on the assumption that chlorophylls b and c would degrade at the same rate after deposition.

The correlation coefficients quoted in Table 22 also indicate that a greater concentration of pigments are found in organic rich sediments. There is a correlation of +0.71 between chlorophyll a and L.O.I. down the whole core and a correlation of -0.60 between chlorophyll a and dry weight. These figures indicate that pigments are associated with relatively higher concentrations of organic matter rather than dry weight. Perhaps this illustrates seasonality of pigment deposition of a limited form in the brown clay gyttja. If the darker laminations were produced under conditions of oxygen stress in the summer, then such conditions are conducive for increased pigment production in upper waters and preservation following deposition to the sediment.

It is apparent that the trend of pigment concentration in L.P.6 is similar to that found in Shagawa Lake, Minnesota (Fig. 23) and Harvey's Lake, Vermont (Fig. 24). Both of these lakes were subject to logging in their catchments and Shagawa Lake to a period of mining which produced haematite-rich sediment. More recently, the two lakes have become increasingly eutrophic. The authors of both

studies concluded that the sedimentary pigments provided a detailed record of the lakes history.

The analysis of sedimentary chlorophyll s in core L.P.6 from Loe Pool also provides a record of past limnological conditions. The concentration of pigments in the sediment profile delimits the periods of mining and eutrophication. The ratio of chlorophyll b:c indicates the relative importance of terrestrial and aquatic pigment sources. There is also evidence from the concentration of sedimentary pigments at Loe Pool to suggest that one or more of the black laminations present were deposited in a summer season.

6.9.2 Chlorophylls, Phaeopigments and Carotenoids in the Black and Grey Laminated Sediment

The absorbance and fluorescence chromatograms of each extract gave a complex mixture of chlorophyll and carotenoid pigments, together with their degradation products (Fig. 76). In order to simplify the presentation of results certain peaks were combined. The concentration of chlorophyll a was added to the allomer of chlorophyll a (chlorophyll a') and the chlorophyll degradation products phaeophytin a, phaeophytin a', pheaophorbide a and chlorophyllide a were combined in a group termed the phaeopigments.

The concentration of chlorophylls a and a' in the black/grey laminated sediments are illustrated in Figures 77 and 78. There appears to be a considerable variation in quantity of pigment

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present. Laminations 1 and 2 from cores L.P.31, L.P.32 and L.P.35 were deposited at the same time. The cores were collected from site A (Fig. 10) the same day, yet the concentration of chlorophyll present varies by a factor of more than 10. If these are accurate results then it suggests that there is not a high uniformity of pigments deposited or preserved across the lake bed.

In six of the varves there is a greater concentration of chlorophyll a and a' in the black than grey laminations. This suggests that the black sediment was deposited during a period of high productivity and under conditions of relatively low degradation. The higher productivity is consistent with a summer rather than winter season. Conditions ideal for the preservation of pigments are rapidly accumulating sediment with anoxic bottom waters. It was suggested by O'Sullivan et al. (1984) that the black laminations may have been formed under anoxic bottom waters. The fact that more pigments are preserved in the black layer corroborates with this suggestion and with other evidence presented in this report that the hypolimnion was anoxic during the summer months.

Both the average concentration and the range of chlorophyll c in the black/grey laminated sediment (Fig. 79) is considerably lower than that for chlorophyll a and a' (Figs. 77 & 78). It was expected that there would be a relatively higher concentration of chlorophyll a than other pigments because it occurs in most higher and lower plants. In contrast chlorophyll c is found mainly in certain algal classes (Table 8). There is a contribution of chlorophyll c throughout the year. This would be expected because the pigment is found in diatoms, a class of algae which are

present throughout the year in Loe Pool (Coard pers. comm.). However, the population of algae does increase in the summer months. Therefore, the higher concentration of chlorophyll c in the black lamination would indicate that this sediment was deposited in the summer season. This bias of chlorophyll c concentration between the black and grey laminations would also be enhanced by anoxia of the bottom waters promoting pigment presentation at the sediment-water interface during the summer months.

There appears to be at least twice the quantity of phaeopigments than chlorophyll a and a' in the black/grey laminations (Figs. 77,78,80 & 81). The phaeopigment profile is similar to that for chlorophyll a and a'. As the phaeopigments are degraded from the chlorophylls it would be expected that their distributions were related. This tends to imply that the high ranges of chlorophyll a and a' and the phaeopigments reported at the start of this section are in fact accurate.

There is a greater concentration of phaeopigments present in each of the black than grey laminations (Figs. 80 and 81). This may be because in the black sediment there is a greater concentration of chlorophylls to degrade to phaeopigments. However, it appears from the phaeopigment:chlorophyll $a + a'$ ratio (Fig. 82) that the production of phaeopigments is relatively higher in the black than grey sediment. The average ratio in the black sediment is 8.0 compared with 5.3 in the grey lamination. This implies that there is some process by which phaeopigments are preferentially produced in the summer relative to the winter.

Some known degradation paths of chlorophylls were outlined in

section 3.8. One possible reason for the preferential production of phaeophytins is grazing by zooplankton. Daley (1973) reported that grazing by Cladocera spp. of blue-green algae containing chlorophyll produced phaeophytins and phaeophorbides in their faeces. Maximum grazing by zooplankton would be expected in the summer months. This is consistent with the greater concentration of phaeopigments in the black laminations.

Phaeophytin may also be produced by acidification. It is possible that this change could occur under anoxic conditions if the waters were sufficiently reducing.

Mechanisms of chlorophyll degradation in lacustrine systems are not fully understood. However, evidence from the laminated sediment formed in Loe Pool indicates that there is a relatively larger concentration of chlorophylls a and a', chlorophyll c and phaeopigments present in the black than grey sediment. This is consistent with deposition of pigments in the summer season to an anoxic sediment-water interface.

The chromatograms of absorbance (for example Fig. 76) show evidence of several carotenoids. For all except two peaks, the concentration of carotenoid was too small to allow identification by a spectral scan. These two peaks occurred in each lamination analysed. The first peak coeluted with the standard fucoxanthin (Fig. 22), but comparison of the absorbance spectrum (Fig. 84) with standards indicated that the peak was caused by another pigment. The average concentration of peak 1 was much lower than peak 2 (Figs. 86 & 87). There did not appear to be any bias of peak 1 between the black and grey laminations. Peak 2 coeluted with the standards lutein and zeaxanthin. The structures of these

carotenoids are illustrated (Fig. 22). Spectral absorbance analysis at several points indicated that Peak 2 was mainly composed of lutein (Figs. 83 & 85), though there was evidence of some zeaxanthin in one very small shoulder.

The carotenoid lutein is reported to have a mainly terrestrial origin (Goodwin, 1976), although it does occur in some algae (Table 10). This suggests that the allochthonous contribution of pigments to the lake is very important. However, it is apparent that there is substantially more lutein present in the black than the grey laminations.

It was noted that the spectrum of Peak 1 (Fig. 84) was similar to that of Peak 2 (Fig. 85), with a hypsochromic shift (shift to higher frequencies, i.e. lower wavelenghts) of approximately 20 nm. This is typical of an oxidation product of a carotenoid (Goodwin, 1980). Carotenoid 5-6 epoxides are widely distributed in nature and form in the presence of molecular oxygen. 5-8 Epoxides (Fig. 22) have also been reported (Goodwin, 1980). They are thought to be rapidly formed from 5-6 epoxides under slightly acidic conditions. Initial evidence (Fig. 84) indicates that Peak 1 may be an oxidation product of lutein. As lutein is the major carotenoid present it would be reasonable to expect some of the degradation products of this carotenoid to be present. If it is assumed that the carotenoid Peak 1 is the 5-8 epoxide of lutein then the ratio of Peak 1:Peak 2 (Fig. 88) indicates that a greater proportion of lutein is degraded to the oxidation product in the grey (winter) than the black (summer) lamination. Assuming that the oxidation product forms more readily in oxidising rather than reducing conditions, then the carotenoid Peak 1:Peak 2 ratio provides

further evidence that the bottom waters in the summer are reducing and in the winter, oxidising.

If carotenoid Peak 1 is not a 5-8 epoxide of lutein then it can only be concluded that the black laminations have a consistently different proportion of Peak 1 than the grey. The ratio Peak 1:Peak 2 provides evidence of a difference between the black and grey laminations, though the reason for this may not be known.

The following conclusions from the analysis of the pigments from the laminated sediment may be made:

1) That the concentration of chlorophylls in L.P.6 delimit periods of mining and the eutrophication of the lake since 1940.

2) That the chlorophyll b:chlorophyll c ratio can be used to illustrate the relative importance of terrestrial and aquatic sources.

3) That analysis of chlorophylls, their degradation products and carotenoids indicated that the black lamination was deposited in the summer under reducing conditions and the grey layer in the winter, when the bottom waters were oxidising.

6.10 Extractable Lipids in the Black/Grey Laminated Sediment

6.10.1 Quantification of Lipid Fractions

It was reported in section 5.10.1 that quantification of extractable lipids by weight was not possible because of contamination by sulphur. The presence of this element provides evidence of sulphate reducing bacteria (Brookes et al. 1976).

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Sulphur is partly soluble in a variety of solvents and so is readily extracted from the sediment with other lipids. It is possible to remove the sulphur from the total extract using either a copper column or shaking with elemental mercury (4.4.8.1). However, a report in the literature (Blumer, 1957) and experience in the use of the techniques suggested that loss of lipid material occurs. In order to avoid such loss, sulphur was only removed from samples prior to urea adduction and C.-G.C.-M.S. analysis. Therefore, it was not possible to quantify each fraction by weight. Instead the major lipids were quantified using a G.C. calibration technique (4.4.8.5).

The results of this quantification step are shown in Table 23. It may have been expected that the concentrations of all lipid fractions would be similar in lamination 1 of each core and again in each lamination 2 because these represent the sediment was deposited at the same time. However, there is a large variation in the concentration of lipids between laminations. This may be caused by one or a combination of the following reasons:

1) Variation in the deposition of lipid material between each core.

2) Variation in the rate of depositon of non-lipid material between each coring site thus affecting the concentration of lipids present.

3) Different degradation rates of lipids in each sediment core.

4) Variation of extraction efficiency between each sediment sample.

5) Differential loss of material in separation processes.

6) Errors in the quantification of lipid.

7) Errors in the quantification of sediment dry weight.

The first three reasons are possible causes of a different lipid

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concentrations in each lamination. Points 4-7 are caused by experimental errors. With most techniques it is possible to allow for such errors. However, the extraction, separation and analysis of each fraction from just one lamination would take approximately two weeks. Therefore, it is impractical to test the errors involved with sufficient samples to calculate a statistical test such as coefficient of variation. The variation in concentrations observed in corresponding laminations, of lipids may be caused by one or a combination of all seven of these reasons.

Comparison of the average concentration of lipid from Loe Pool and two other freshwater eutrophic English waterbodies is made in Table 26. There is a higher concentration of most fractions in the sediment from Esthwaite Water and Rostherne Mere, than Loe Pool. There are 2 possible reasons for this:

1) Productivity was greater in both Esthwaite Water and Rostherne Mere than in Loe Pool when the sediment was deposited.

2) That sediment in Loe Pool was diluted by a greater proportion of minerogenic matter than in the other lakes.

It should be noted that the figures presented in Table 26 are based on surface sediment from Esthwaite Water and Rostherne Mere whereas the laminations from Loe Pool had been buried for approximately 50-60 years. Hence a direct comparison with surface sediment at other sites must be treated with caution because of possible differences caused by degradation with time.

From the comparison of the lipid concentration in the black/grey varves sampled from Loe Pool, with sediment from other sites, the following conclusions may be made:

Lipid composition of lacustrine sediment g/g dry sediment			
Lake	Alkanes and alkenes*	Alkanoic acids*	Reference
Loe Pool[@]	8.0	25.2	This study
Rostherne Mere 0-7 cm.	40.5	155	Brooks et al., 1976
Esthwaite Water 0-5 cm.	67	24	Brooks et al., 1976

[@] average composition of black/grey laminated sediments
* all amounts estimated . by G.C. response of pre hydrolysis extract

Table 26. Comparison of lipid concentration between Loe Pool and two other lacustrine sediments.

1) That there was a low proportion of extractable lipids deposited during the 1920's and 1930's in Loe Pool.

2) That Loe Pool has become increasingly eutrophic since the cessation of mining.

These are consistent with conclusions reached from the results of other physical and chemical properties discussed in this study.

It was postulated in section 3.9 that there may have been higher concentrations of extractable lipids deposited in the black than the grey laminations. This was because of increased productivity during the summer months. However, the variation of lipid concentration of laminations analysed is too large to allow comparison between the black and grey sediment.

6.10.2 Normal Alkanes

The n-alkanes from each lamination analysed exhibited a major mode at n-C 31 (Figs. 93 & 94). This is indicative of a terrestrial input (Cranwell, 1977b). The range of n-alkanes in Loe Pool sediments have a greater similarity to those from Loch Clair (Fig. 26) than Rostherne Mere (Fig. 27). The Loch Clair sediments are dominated by input from an allochthonous source and consequently have an n-alkane range of C 17 to C 35 in a unimodal distribution with the maximum peak at n-C 31 and a C.P.I. greater than 5. In contrast, the eutrophic Rostherne Mere sediment has a bimodal distribution around n-C 29 and n-C 17.

Each bar chart (with the exception of L.P.35 lamination 2) does show a small secondary peak around n-C17 (Figs. 93 & 94). These

are indicative of an aquatic input (section 3.9.3.1).
Shorter-chain length alkanes are degraded preferentially compared
to longer-chain lengths (Giger et al., 1980). It is possible
that the proportion of n-C 17 was higher in the sediment at the
time of deposition than it is now.

There are no consistent differences between the n-alkane range in
the black and grey laminations. It was noted in the results
(5.10.2.) that the average C.P.I. of the black sediment was 4.4 and
the grey sediment 5.4. Cranwell (1982) suggested that the C.P.I.
value can be indicative of source. A high value being
characteristic of terrestrial plants and lower values typical of
microbial activity. It is apparent that lipids from higher plants
dominate the extractable n-alkanes in Loe Pool sediment throughout
the year although they are relatively more important in the grey
than the black lamination. This is consistent with the hypothesis
that the grey sediment was deposited in the winter months when the
input of terrestrially derived matter was considerable.

It may be concluded from the n-alkane sediment range and C.P.I. of
the black and grey laminations that, the organic matter within the
sediment has a principally allochthonous source, and that in the
1920's and 1930's the lake was probably not highly productive.

6.10.3 Branched and Cyclic Hydrocarbons

It was proposed in the introduction to the branched and cyclic
hydrocarbons (3.9.3.2) that the pristane:phytane ratio may be used
in the identification of palaeo-redox conditions in recent

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lacustrine sediments. This idea was first tested by running chromatograms of the non-adduct hydrocarbon fraction from each extract. Each chromatogram included peaks 1 and 2 (Fig. 95) which were thought to be pristane and phytane by co-chromatography with authentic standards. Mass fragmentogram and mass spectral data, however, have indicated that the major components of peaks 1 and 2 are not pristane and phytane (Figs 96,97,98,99,101 and 102).

Mass spectral data from this work concurs with the conclusion reached by Robson et al. (in prep.). The authors reported that caution must be exercised in identifying pristane on the basis of retention time data alone. This is because of the co-elution of pristane with a widely distributed C 20 branched alkane (Fig. 100).

It was noted in the results of the straight-chain hydrocarbons (5.10.2) that there was no appreciable unresolved complex mixture (U.C.M.). Conclusions from such an observation are that the sediment did not appear to be polluted by oil or petroleum (Douglas et al., 1981). This point was strengthened by examination of sedimentary hopanes. Mass fragmentogram and mass spectral information indicated the presence of 2 dominant hopanoids (Figs 103, 104, 105 & 106). Work by Dastillung and Albrecht (1976) has shown that the level of oil pollution may be gauged by the presence of hopanes. Jones (1986) reported that the saturated fraction of an unpolluted sediment extract was dominated by a C 31 hopane (Fig. 122). These are thought to be indicators of bacterial activity (Ourisson, 1979). In contrast, a lipid extraction from an oil polluted sediment contained a series of hopanes occurring in characteristic doublets (Fig. 121). Comparison of the M/Z 191
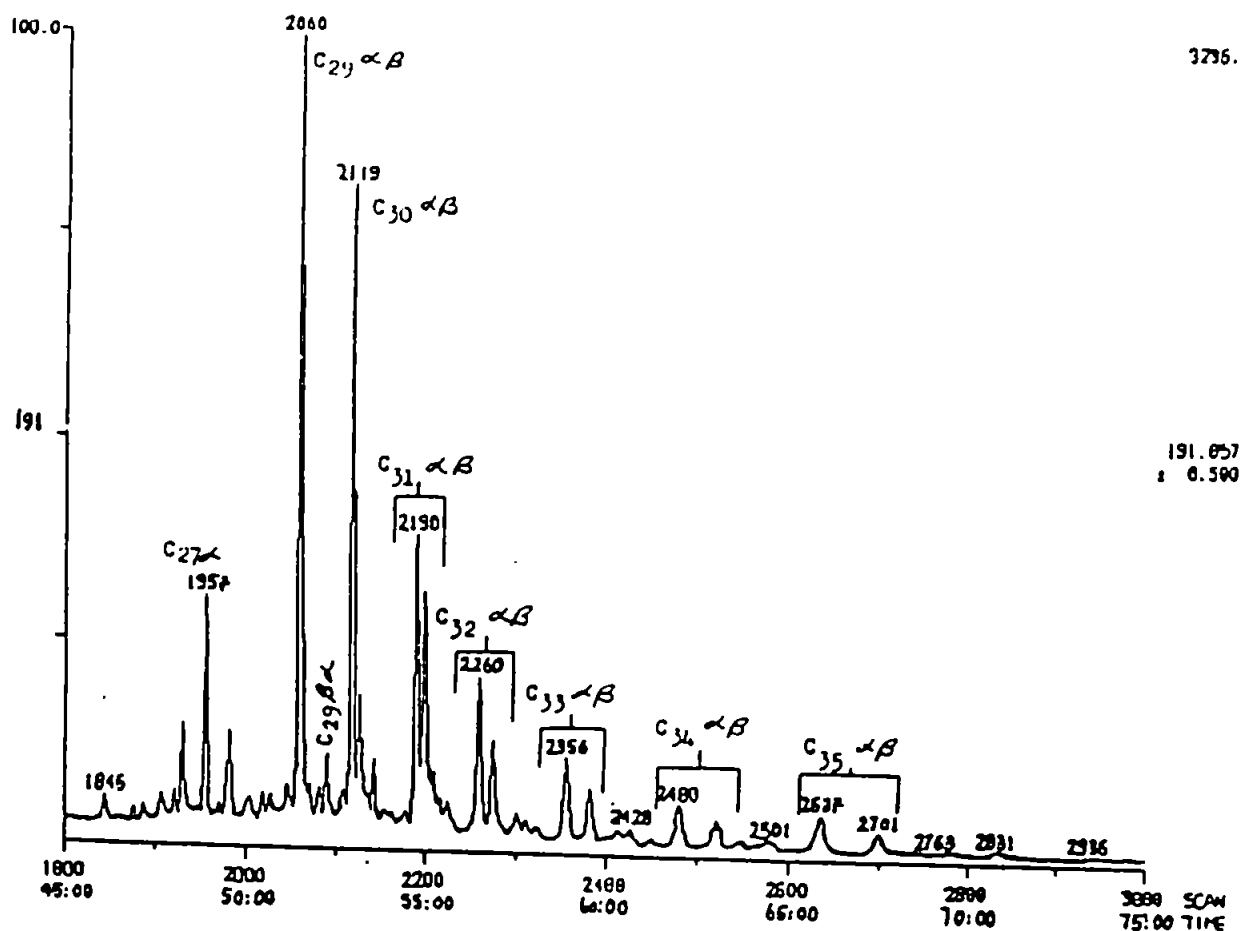
Figure 121. M/Z 191 Fragmentogram (Scan numbers 1800 to 2800) of the saturated alkanes isolated from an oil polluted marine sediment. Pertacyclic triterpanes of the hopane family are denoted by their individual carbon numbers (from Jones, 1986).
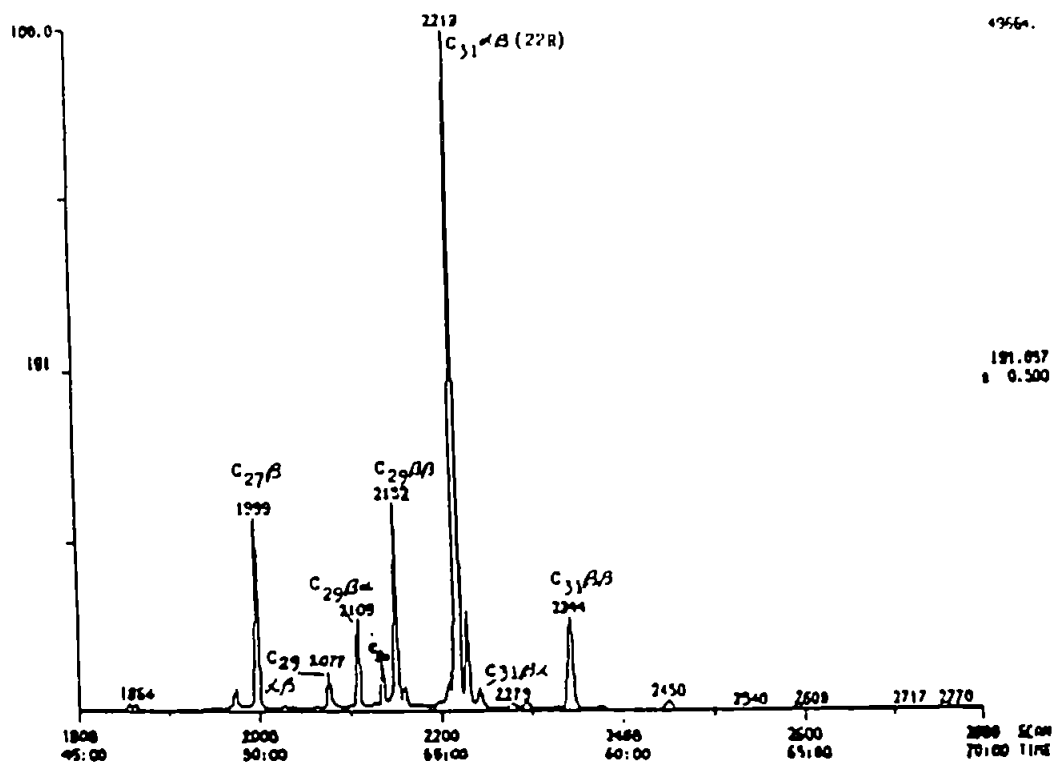
Figure 122. M/Z 191 mass fragmentogram (Scan numbers 1800-2800) of the saturated alkanes isolated from an unpolluted marine sediment. Pentacyclic triterpanes of the hopane family are denoted by their individual carbon numbers (from Jones, 1986).

fragmentogram of the hopanes and hopenes in Loe Pool (Fig. 103) revealed only one major hopane and one major hopene. The similarity between the extract from Loe Pool and the unpolluted marine sediment suggests that the black/grey laminations are unpolluted with respect to oil.

In the introduction to the branched/cyclic hydrocarbon fraction (3.9.3.2) it was noted that several authors had reported the presence of 7- and 8-methyl heptadecanes. There were no detectable quantities of these compounds in the fraction analysed.

It may be concluded from analysis of the branched/cyclic hydrocarbon fraction that there were no specific indicators of either aquatic or terrestrial sources. In addition, there is evidence of bacterial activity, but no apparent oil pollution. The presence of C-20 branched alkanes prevents the calculation of a pristane:phytane ratio and hence the identification of palaeo-redox conditions.

6.10.4 Alkyl esters

The range of n-alkyl esters extracted from Loe Pool sediment was from C 34 to C 48 peaking at n-C 44 (Fig. 107). Comparison with results from other studies (Figs. 28 & 29) indicate that this range is consistent with a higher plant source (Cranwell & Volkman, 1981). The grey lamination contained a series of branched esters which may be attributed to microbial action (Cranwell, 1983). It is not known why there should greater microbial activity in the

grey than the black lamination. Microbial activity is generally associated with warm, organic and nutrient rich environments. There is no reason to suppose that such differences existed between the black and grey laminations.

6.10.5 Polynuclear Aromatic Hydrocarbons

The polynuclear aromatic hydrocarbons (P.A.H.) fraction extracted from each lamination examined is dominated by perylene (for example Figs. 112 & 113). Some P.A.H. have been reported as characteristic of anthropogenic activity (Wakeham, 1980). The concentration of other P.A.H compounds in Loe Pool sediment was below detection limits. This indicates that the black/grey sediment was not polluted by fossil fuels and their combustion products. This conclusion is in agreement with results from the analysis of the branched/cyclic hydrocarbon fraction (6.10.3).

Evidence from the literature cited in 3.9.5 indicates that perylene is the major P.A.H. at many sites. The origin of the compound is unknown though Louda and Baker (1984) report that sedimentary perylene concentrations are highest where the overlying waters are productive and the hypolimnion is anoxic. In Loe Pool sediment perylene concentrations were found to be highest in the black lamination of three of the four varves. (Figs. 114 & 115). This suggested that the lake was more productive and the bottom waters were anoxic during deposition of the black laminations. This conclusion is in agreement with other evidence that indicates that the black sediment formed during the summer months

under conditions of oxygen shortage. However care should be taken not to put too much weight on this conclusion, because the results are only presented for four varves and the precursor organism and mode of formation of the compound perylene are unknown.

6.10.6 Normal Alkanols

The n-alkanol distribution in Loe Pool sediment is from C 22 to C 28 maximising at C 26 with a C.P.I. of 4.5 to 9.1 (section 5.10.5, Figs. 110 & 111) is characteristic of a higher plant contribution (Cranwell, 1977). The chromatograms reproduced (Figs.110 & 111) are similar to those for Loch Clair (Fig. 26) which has a predominantly allochthonous source of organic matter. There is no indication of a strong secondary mode around n-C 16 as found in the sediment from the eutrophic Crose Mere (Fig. 30).

There are two noticeable differences between the distribution of n-alkanols in the black and grey laminations. First, that the C.P.I. is higher in four of the black than the grey laminations. The reason for this is unknown. Secondly, that the ratio of n-C 26:n-C 28 is higher in the black lamination for all the varves analysed (Table 24). In oligotrophic Loch Clair, n-C 28 is the most abundant alkanol and in Cam Loch (also oligotrophic) either n-C 26 or n-C 28 dominates (Cranwell, 1977; Cranwell, 1981). In contrast, in the eutrophic Crose Mere, n-C26 is the dominant alkanol throughout the range. Possibly n-C 26 is relatively more important than n-C 28 in lakes with a high autochthonous input and n-C 28 occurs in a higher proportion than n-C 26 in lakes where an

allochthonous contribution is more important.

At Loe Pool the black lamination has a relatively higher n-C 26:n-C 28 ratio than the grey . Possibly this indicates that the black and grey laminations were deposited during periods of maximum autochthonous and allochthonous deposition respectively. This is compatible with the notion that the black sediment was deposited at the time of greatest aquatic production during the summer, and the grey lamination formed during the winter when allochthonous input is highest.

It may be concluded from the distribution of n-alkanols in Loe Pool sediment that:

1) An allochthonous source dominated the input of organic matter during the 1920's and 1930's.

2) That the C 26:C 28 n-alkanol ratio is higher in the black than the grey laminations. It is possible that such a ratio might be used as an indicator of the proportion of allochthonous:autochthonous organic matter in the sediment.

6.10.7 Alkanoic Acids

The alkanoic acids in the black/grey laminated sediment formed in Loe Pool had a distribution in either 1 or 2 modes around n-C 16 and n-C 26-30 (Figs 119 & 120). Literature reviewed in section 3.9.3.6 suggested that the source of the n-C16 fatty acids is probably microbial or algal and the n-C 26 to n-C 30 fatty acids had an origin of higher plant material.

There is no regular variation in the n-alkanoic acid distribution

between the black and grey laminations. In two of the varves there is a relatively higher microbial/algal source in the black lamination and greater terrestrial plant contribution in the grey layer. This is consistent with an increase in the proportions of aquatic production in the summer months when the black sediment was formed and with the deposition of higher plant matter in the winter during the sedimentation of the grey lamination. However, no conclusions regarding the use of alkanoic acids to differentiate between lipid source can be made because the opposite trend was evident in L.P.32 lamination 5 and 6 (Fig. 120).

The potential information from the distribution of n-alkanoic acids is limited by the absence of compounds from extracts of L.P.32 laminations 1 and 2. This absence is probably caused by degradation either before or after extraction, as alkanoic acids are known to be more labile than many other lipid fractions (Cranwell, 1981). The only firm conclusion that can be made from the analysis of n-alkanoic acids from Loe Pool is that these compounds reveal a microbial/algal and/or higher plant source of organic matter in the sediment . Possibly more information could be gained by a quantitative study of the other acid compounds shown to be present in the individual laminations (Fig. 116).

Chapter 7 Conclusions

It was stated in section 1.4 that "the sediment which accumulates in lakes can be likened to a data storage bank holding records of past conditions and events in the water body and drainage basin." The aim of this project was to investigate selected chemical and physical properties of individual laminations deposited in Loe Pool sediment in order to reveal information held "on file" in the sediment.

7.1 Source of the Laminated Sediments Formed in Loe Pool

Evidence from analysis of combustion residue (C.R.) suggests that more than 80% of the sediment formed was minerogenic. This figure is likely to be higher because comparison of the % loss on ignition (section 5.3.3 & section 5.3.4) and organic carbon (Fig. 69) indicated that much of the other 20% of material was water. Some of the mineral fraction will have been formed within the lake, for example, the precipitation of carbonates. Despite this, it may be concluded that most of the mineral matter within the sediment has a terrestrial origin.

The % combustion residue was greater in the black/grey and black/red laminations analysed, than in the top brown clay gyttja sedimentary unit. The concentrations of copper, zinc and other heavy metals, together with the evidence of a high haematite content from analysis of magnetic variables from the black/grey and

black/red laminated sediments concur with historical evidence of mining activity during the 1920's to 1930's. It is evident that a terrestrial source of material was particularly important when the mines were operating.

A further indication that the mineral matter in Loe Pool sediment has a terrestrial origin is the low concentration of organic carbon and nitrogen. Other freshwater sediments had typically 5 times as much organic carbon and nitrogen than the varves formed in Loe Pool (Table 17). This low concentration of organic carbon and nitrogen in the black/grey laminated sediment was attributed to dilution caused by the deposition of clastic material.

Analysis of the extractable lipid component of the organic material also indicated a principally terrestrial source. The major portion of the n-alkane, n-alkanol and n-alkyl ester fractions each contained a range typical of higher plant lipids. It may be concluded from the analysis of various chemical and physical properties of the laminated sediments formed in Loe Pool that the major source of material is allochthonous.

7.2 Season of Sediment Deposition

Analysis of diatom remains in the black/grey laminated sediment showed that the black lamination was formed in the summer and the grey layer in the winter (Simola et al., 1981). Several of the chemical variables investigated in this study support this conclusion. The pigments, chlorophyll c and the phaeopigments, each had a higher concentration in the black than grey laminations. This would be expected in the summer when aquatic productivity and

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grazing by zooplankton are at a peak. The C:N ratio is lower in the summer, consistent with a greater algal input and higher in the winter when terrestrial plant material is a more important source of organic matter.

Finally, there was a higher concentration of perylene produced in more of the black than the grey laminations. Evidence cited from the literature suggests that perylene has a higher concentration in sediments where the overlying waters are both productive and anoxic. This is consistent with the formation of the black sediment in the summer months.

7.3 Palaeo-Redox Conditions

Some of the most striking differences between the black and grey laminations were the Fe:Mn ratio, the concentration of calcium and the % carbonate. The variables calcium, carbonate and manganese are readily soluble in anoxic (reducing) conditions. The low carbonate and calcium levels and high Fe:Mn ratio in the black sediment are consistent with reducing conditions. In contrast, the grey sediment has significantly higher concentrations of calcium and carbonate and a lower Fe:Mn ratio which may occur when these compounds precipitate to the sediment under oxidising conditions. Evidence from the ratio of carotenoid peak 1:peak 2, and the concentration of perylene and humic acids in the sediment also suggest that the black lamination formed under reducing conditions and the grey layer in oxygenated water. The notion that the black sediment was formed under reducing conditions is further strengthened by

evidence summarized in section 7.2 that indicates that this lamination was deposited in the summer months.

Many temperate lakes typically form reducing conditions in the bottom waters during the summer months (Wetzel, 1983). During this period the lake is usually relatively still and because of the precipitation of organic matter there is a high oxygen demand. Previous work at Loe Pool has indicated that oxygen stress occurred at the sediment-water interface in the summer months. It was thought that anoxia would have been even greater in the past when the lake was deeper. From the evidence summarized in this section it may be deduced that the black laminations were deposited under reducing conditions and the grey laminations were formed when the bottom waters were oxygenated.

It is concluded that by the analysis of selected chemical and physical properties of the individual black and grey layers deposited in Loe Pool it is possible to identify the main source of sediment and the season and palaeo-redox conditions under which each lamination was formed.

7.4 Hypothesis for the Formation of the Laminated Sediments
Deposited in Loe Pool.

In the introduction to a paper entitled "The record of a lake's life in time: the sediments" Pennington (1981), states with reference to the analysis of lake sediments that "the data are explained by construction of hypotheses, which interpret these facts in terms of the state of the lake in the past, using knowledge of the composition of the sediment accumulating today in

lakes of different types in different climatic regimes." From previous work (Simola et al., 1981; O'Sullivan et al., 1982; Coard et al., 1983, O'Sullivan et al., 1984; and Coard, in prep.) and work presented in this study a tentative hypothesis is formulated to explain the occurrence of the different stratigraphic units reported by O'Sullivan et al. (1984) and illustrated in Figure 2.

The brown clay at the base of the sediment profile was deposited prior to the onset of extensive mining in the catchment. The diverse diatom flora reported by O'Sullivan et al. (1984) also indicates that pollution by mine waste was low. The lake was probably well mixed because of frequent bar breaking and possibly by marine incursions. The combination of these two factors could have prevented the formation of anoxia in the bottom waters during the summer. This sediment is not coloured by black metallic sulphides and supports benthic activity shown by bioturbation. This is further evidence that the bottom waters of Loe Pool were fully oxidised. It is not known why the irregular fine grey laminations formed.

Towards the end of the eighteenth century two new factors influenced the formation of sediment within Loe Pool. One was the gradual increase in the level of mining in the catchment. This activity increased the minerogenic sediment load. The second factor was the opening of the drainage "adit" which controlled the lake level. This stabilization of the water depth may produce conditions conducive to the formation of anoxia during the summer in the bottom waters.

From studies of the English Lakes Pennington (1981), notes the

following conclusion by Mortimer (1941): "in the shallow lakes in which chemical evidence suggests an early development of some degree of anoxia in the summer, the accelerated reduction in volume of the hypolimnion would be expected to intensify the development of reducing conditions at the mud-water interface......"(p. 211 and 213). It may be concluded that the gradual stabilisation of the lake depth and increase in erosion from the catchment, so reducing the volume of the hypolimnion, allowed conditions of anoxia to develop in the summer months. The high sedimentation of toxic mine waste and seasonal anoxia killed off the benthic fauna, so ending bioturbation of the sediment. It is proposed that the combination of the input of mine waste and stabilisation of the lake level allowed the formation of seasonal anoxia and hence the development of the black/grey varves. This pattern was only interrupted by the occasional massive deposition of haematite producing pinky-coloured bands instead of the grey. The increased stability of the bar and the improvement in the "adit" through which water flowed from the 1850's promoted the formation of these black and grey laminated sediments.

The formation of the black/grey laminations was broken in the 1930's, when increased mining activity produced massive quantities of sediment. Simola et al. (1981) suggested that up to 80cm of sediment was deposited in 7 years. In a paper by Deevey (1955), the author stated that the hypolimnion of shallow basins may be obliterated by rapid deposition of sediment. This probably happened in Loe Pool around the 1930's. The lake became so shallow that prolonged seasonal anoxia did not occur in the bottom waters. The sediment deposited throughout the 1930's is mainly coloured grey

and pink. This primarily reflects the input of minerogenic matter.

The cessation of mining reduced the input of mineral erosion from the catchment. The result was a change in quality of sediment to a brown clay gyttja. From 1940 the lake was too shallow to form prolonged anoxia in the bottom waters so the brown rather than the black sediment developed. Because the lake no longer received mine waste, benthic fauna were able to become re-established in many parts of the lake. Such organisms are not conducive for the formation of laminations because they tend to mix the sediment deposited by burrowing. However, some sections of the stratigraphic unit exhibited the presence of laminations (for example core L.P. 6). The mode of formation of these is unknown.

In the most recent sediment Simola et al. (1981) reported a series of 4 or 5 pairs of light and dark brown laminations. In contrast to the black/grey varves formed from 1815 to 1930, evidence from the diatom flora indicated that the light coloured sediment was deposited in the summer months and the darker layer in winter. Possibly this is the start of a seasonal deposition of carbonate in the summer months. Such a process was suggested by Peglar et al. (1984) as a response to either increased water temperature or algal production. Carbonate formed would have been able to deposit on the surface of the sediment post 1940 because of the absence of anoxic conditions in the bottom waters.

In the introduction to section 7.4 some text from a paper by Pennington (1981) was quoted. This author continues her text as follows: "the advantage of multidisciplinary work on sediments is that possession of different kinds of data for the same sediment

profile enables palaeolimnologists to apply rigorous tests to hypotheses—only those which satisfactorily explain all sets of data can be true. This testing is the palaeolimnologist's equivalent of experiment, for which human life is too short." The work presented in this thesis attempts to cover a wide range of chemical and physical techniques. By necessity the time available for each analysis is too small. However, the combination of this limited amount of information from each technique has enabled the construction of a hypothesis for the formation of the laminated sediments in Loe Pool.

7.5 The Use of Physical and Chemical Techniques in the Investigation of Laminated Sediments.

The overiding aim of this project was to highlight those techniques which had the greatest potential for the elucidation of information from laminated sediments. However, the strength of the multidisciplinary approach is that conclusions from many variables studied may be combined to reveal more information from the lake-sediment data base, than can be obtained using just one technique. Therefore, it must be concluded that no one technique should form the basis of sediment analysis. However, the investigation of different physical and chemical variables of sediment requires different levels of scientific expertise, time to perform and equipment to use. As a basic reference to future palaeolimnological studies a summary of certain aspects of each of the techniques reported in this work are presented in Appendix 1.

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Appendix 1

Summary of Aspects of Each Technique Used of Relevance to Palaeolimnologists

Dry weight	Techniques easy to use and gain
Loss on ignition	rapid results. The information is
Combustion residue	essential in the analyses of other
	variables and in interpreting all
	data.

Magnetic susceptibility	Techniques require understanding
S.I.R.M.	of magnetism, method is easy and
S ratio	quick to use. The results have
Susceptibility/S.I.R.M.	limited application in comparison
	with some other variables. Access
	to specialised equipment is
	essential.

Analysis of	Knowledge of inorganic geochemistry
metals	and some skill in the operation
	of analytical equipment are
	required. The method is relatively
	quick and can provide useful
	information. The Fe:Mn ratio can be
	a particularly useful parameter in
	the study of laminated sediments.

Determination of organic carbon and nitrogen	Some knowledge of chemistry needed to comprehend fractionation of carbon. Analysis easy and quick to perform. Care is necessary in the calibration of the instrument. The C:N ratio can provide an an indication of the sediment source.
Quantification of humic acids	Difficult and lengthy technique to perform.
Analysis of carbonate	Technique can be performed simultaneously with determination of organic carbon and nitrogen. The concentration of sedimentary carbonate can be an indicator of palaeo-redox conditions.
Extraction and spectrophometric analysis of pigments	Care is required in extraction and determination of all pigments because of their lability. The method can be lengthy and results gained should be treated with considerable caution.

H.P.L.C. analysis of pigments	In addition to the above technique a working knowledge of analytical chromatography is required. Some specialised equipment is needed and the method from separation to analysis and quantification requires a considerable length of time. The technique has the potential to reveal data which may indicate the season of deposition or source of the sediment.
Extractable lipids	This technique requires a detailed understanding of organic geochemistry. The extraction, separation and analytical processes are very time consuming. In addition, great care must be taken with each step to avoid loss of and contamination to the extract. There is tremendous potential for gaining information of importance to palaeolimnologists. Specialised equipment is required to separate and identify many of the lipid fractions.

Appendix 2

List of Papers Contributed to during the course of this Research Programme

Coard, M.A., Cousen, S.M., Cuttler, A.H., Dean, H.J., Eglinton, T.I., Greaves, A.M., Lacey, K.P., O'Sullivan, P.E., Pickering, D.A., Rhead, M.M., Rodwell, J.K. & Simola, H. 1983: Paleolimnological studies of annually-laminated sediments in Loe Pool. Hydrobiologia, 103, 185-191.

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