LAGO GRANDE DI MONTICCHIO: A PALAEOENVIRONMENTAL RECONSTRUCTION FROM SEDIMENT GEOCHEMISTRY

by

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DECLARATION

I certify that the work presented in this thesis is my own, except where otherwise stated and has not been presented for a degree at this, or any other university.

ABSTRACT

During 1990 a 51 metre core was recovered from Lago Grande di Monticchio, a maar lake in S Italy. This provides a high quality laminated sequence extending back into the Late Quaternary which is being examined by a multidisciplinary group. The project here is concerned with sediment geochemistry as a tool for reconstruction of palaeoenvironmental conditions at this locality.

The core was analysed at 10cm resolution using techniques such as X-ray fluorescence (XRF). This has produced a highly detailed record of change reflecting either the last 70,000 or 220,000 years. Organic carbon and biogenic silica are believed to represent biogenic productivity and, in particular, nutrient status in the lake system. It is found that the Holocene is marked by very high concentrations of these components in contrast to the minerogenic glacial sediments. Possible earlier interglacials (e.g. the Eemian) contain significantly lower contents of biogenic matter, suggesting that nutrient conditions may have been somewhat poorer during these times. Alternatively, these periods could represent interstadials within the last glacial cycle. C/N ratios and Hydrogen Index values probably reflect both the source and degree of preservation of the organic matter, but should be interpreted cautiously. The $\delta^{13}C$ record for bulk organic matter shows a significant shift to isotopically lighter values during the glacial-Holocene transition, but the profile is difficult to interpret due to the many possible factors involved.

Indicators of terrigenous clastic material show that the late-glacial and Holocene sediments have received relatively base-rich clastic material probably derived from contemporary tephra inputs to the catchment. This is marked by ratios such as Na/Al and K/Al which increase in apparent association with increased tephra deposition and Zr/Rb which decreases. The effect of tephra blanketing of the catchment and subsequent release of nutrients is proposed as a cause for the much higher productivity during the Holocene interglacial. A second factor, lake infilling and consequent enhanced nutrient recycling, provides a further reason for increased productivity with time. These two factors are independent of climate which has generally been considered as the main driving force.

A variety of diagenetic phases are present, including vivianite, pyrite, calcite and siderite. The latter is sometimes Mn-rich and the associations of these phases often over mm-scale intervals in the sediment are used to reconstruct possible diagenetic regimes in the lake.

Organic geochemical investigations are at an early stage, but so far show a dominance of higher plant n-alkanes in the sediment record, possibly a result of selective preservation. Palynofacies examination of the organic matter indicates that the Holocene and, to a lesser extent the earlier interglacial (or interstadial?) horizons contain relatively fresh algal and plant material together with an abundance of insect and pollen remains.

The geochemical composition of the core may be summarised by multivariate data analysis and such a summary is used to correlate the record against the marine oxygen isotope curve. From this, a speculative reconstruction can be made of sedimentation rates for the Holocene (0.75mm/year) and for earlier periods (generally <0.25mm/year). It is emphasised that such interpretations require the support of objective dating to gain in value.

CONTENTS

LIST OF PLATES

Plate 1. Fieldwork at Monticchio during Sept 1990

CHAPTER 1

INTRODUCTION

The Quaternary Period

The Quaternary covers approximately the last 2 million years of earth history (Lowe and Walker, 1984; Bowen, 1978). It has been characterised by dramatic changes in climate occurring over relatively short geological time scales. The best known example of this perhaps being the Ice Ages which have affected the European continent and further afield. The Quaternary period is also influenced by the effects of volcanism and tectonic movements (typically on a more regional scale) and by the emergence of man. In addition to providing evidence on the past, the Quaternary would seem the most appropriate place to act as a key to understanding how future environments might develop.

Information concerning the Quaternary is available from geomorphological features in glaciated terrains and from depositional records such as marine sediments, fluvial or lacustrine sediments and ice accumulations. Also available are records preserved by organisms such as ancient tree rings and coral skeletons. Much information has been deduced from this broad range of material, but the increasing demands of science encounter several recurring problems:

1) it is often difficult to obtain a record covering the desired length of time or, if the coverage is available, then it may not be of high enough resolution
2) many of the changes recorded are rapid and difficult to tightly constrain with the dating techniques available.
3) it is desirable to produce *quantitative* information (e.g. "how warm actually was it?"). This has been achieved with some success from oxygen isotope values on foraminiferal skeletons and from certain palynological records, but may be very difficult to obtain from many of the geological products that are available for study.

In an attempt to gain maximum information a multidisciplinary approach is often applied with a variety of scientists examining the sedimentological, biological, chemical, anthropogenic and many other aspects of a record. This combined information can then be synthesised and an overall reconstruction produced.

Records and theories of climatic change

Perhaps the best known evidence for climatic change on a 10^5 to 10^6 year time scale is derived from the marine oxygen isotope record (e.g. Imbrie et. al., 1984). δ^{18}O stratigraphy, as a combined record of ocean surface temperature and global ice volume, has provided crucial support for the astronomical theories of glacial-interglacial change which were conceived during the early part of this century (Berger, 1988; Kukla et. al., 1981). The so-

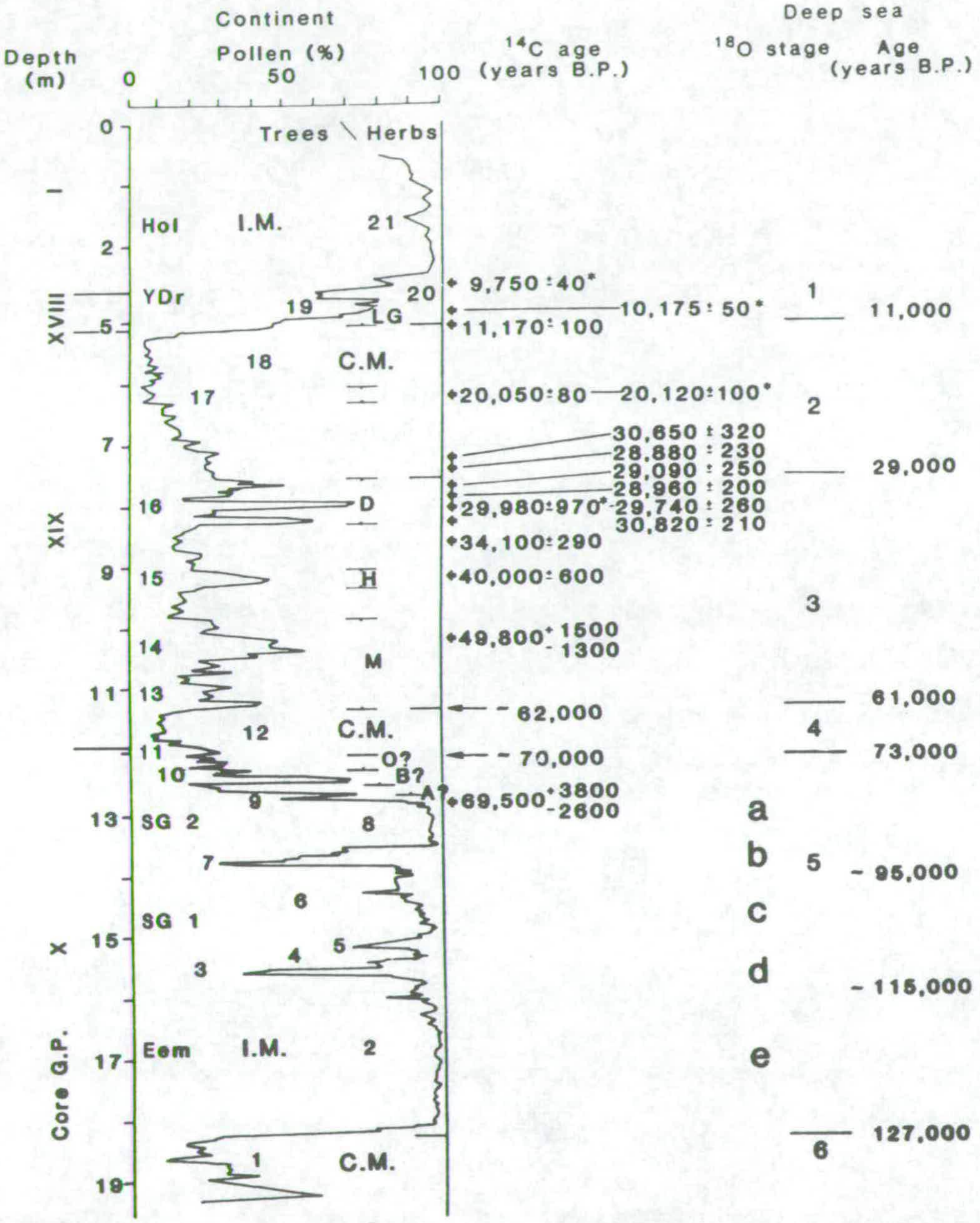


Fig. 1.1. Correlation between the land pollen record from La Grande Pile in eastern France and the marine $\delta^{18}O$ record (Woillard and Mook, 1982)

called Milankovitch theory which involves sinusoidal changes in insolation received at the earth's surface resulting from changes in the earth's orbital parameters has been widely embraced and received little serious challenge over the last 20 years (Winograd et. al., 1992). It predicts that the degree of insolation received should oscillate with frequencies of 100,000, 43,000, 24,000 and 19,000 years. A direct sinusoidal forcing effect on global climate has been argued against however. It is thought more likely that the changes in insolation induce responses in the ocean-atmosphere circulatory system which then directs climatic change in a broadly saw-toothed pattern (Broecker and Denton, 1989). Although the glacial-interglacial changes provide a dominant signal in the Quaternary, other more abrupt changes are observed in detailed proxy records (Berger and Labeyrie, 1987). For example, the Younger Dryas period (Broecker, 1992; Fairbanks, 1989), the Dansgaard-Oeschger cycles of polar ice core records (Johnsen et. al., 1992) and Heinrich events in the North Atlantic (Bond et. al., 1992) have been recognised within the broader glacial cycles. These do not receive direct explanation by the orbital model and may be considered as representing jumps or fluctuations which are a natural part of the ocean-atmosphere system (Broecker and Denton, 1989).

Non-marine long records of palaeoclimate have been obtained from the polar ice sheets and on the continents from lake sediments, loess accumulations and peat deposits. In the case of continental records palynology has provided the main indicator of past climate with stable isotopes and sedimentology used to a lesser extent. It has been possible to correlate these records with the marine oxygen isotope curve on the broad glacial-interglacial level (Jouzel et. al., 1987; Kukla, 1989; Heuser and Heuser, 1990; Adam and West, 1983; Guiot et. al., 1989). This is illustrated in Fig. 1.1. which shows a correlation between the (radiocarbon dated) pollen record from the Grande Pile site in eastern France and the marine oxygen isotope record for the past 130,000 years. However, attempts to correlate *shorter* term changes have met with varying degrees of success. For example the Younger Dryas event is now widely accepted as affecting a large area of the northern hemisphere and perhaps beyond (Wright, 1989). However the Dansgaard-Oeschger cycles seen in the Greenland ice sheet have not been unequivocably correlated with terrestrial records (Broecker et. al., 1988) and Heinrich events seen through ice rafted detritus in the NW Atlantic have only received preliminary associations with the terrestrial pollen record (Grimm et. al., 1993).

In order to improve our knowledge of how these climatic changes operate it is necessary to recover high resolution and long records which can be correlated with established marine profiles. The continents provide a potentially valuable source of information in their relatively high rates of sediment accumulation and their sensitivity to factors such as temperature and rainfall change. As well as climate, other effects such as tectonics and man may influence a proxy record in time and space. Volcanism too can affect some records both in terms of extraneous contributions of material (Kurenkov, 1966) and perhaps through short term forcing of climate itself (Chester, 1989). It is desirable to unravel these effects from the processes of longer term climatic change to achieve a maximum understanding of Quaternary environmental change.

Lake sediments as a proxy record

Lake sediments have long been recognised as providing detailed geological records of environmental change, both in terms of the variety of facies that they can display and their sensitivity to changing climate (Allen and Collinson, 1986). Under favourable conditions it may be possible to reconstruct with an annual resolution for at least the last 13,000 years of earth history (Negendank and Zolitschka, 1993a). This presents an unparalleled opportunity to solve problems such as the nature and timing of the Younger Dryas event (Lotter, 1991a).

Brief review of previous work

Notable early studies concerning lakes and lake sediments include the appreciation of varves (de Geer, 1912) and sedimentation processes in lakes (Lundqvist, 1925). Also at this time Bradley published a great number of ideas from studies on the Green River formation in Wyoming (e.g. Bradley, 1929). Among this work he envoked a hypothesis of Milankovitch-type cyclic control on sedimentation.

A major consolidation of theory concerning lakes came about during the 1950's. At this time Hutchinson published the first volume of his treatise on Limnology (Hutchinson, 1957). He, and later workers such as Deevey, combined limnological theories with palaeolimnological investigations of sediment cores. Over the next two decades they characterised sediment geochemistry and used their data to make basic interpretations concerning changes in sedimentation (Hutchinson and Cowgill, 1963; Hutchinson, 1970). Also, work was well underway in the English Lake District through initiatives by Mortimer and others. (A recent review of the Lake District studies is given by Pennington, 1991.) The mid-1950's also saw the appearance of a devoted journal to the subject -'Limnology and Oceanography'.

In addition to continuing work by groups associated with Hutchinson and Deevey, some influential theories were crystallised from the 1960's Lake District studies. Mackereth (1965; 1966) measured a wide range of elements in sediments from a range of Lake District sites and offered more advanced interpretations of the compositional changes seen. He found that glacial lake sediments consisted wholly of mineral clay, often laminated. Overlying these, post-glacial sediments contained a high percentage of organic matter which must have originated photosynthetically either on the land surface or in the lake waters. These two lithologies can be seen in lakes across many parts of Europe. He regarded the sediments as representing an accumulation of debris (or soils) derived from the land surface with minor additions from the lake biomass. The latter would influence diagenesis and the precipitation of certain elements in the sediment. Consequently the information obtained from a study of lake sediments should mainly be concerned with events affecting the surrounding land surface, and to a lesser extent with conditions in the lake itself. Mackereth assumed that no *major* post depositional diffusion of elements had taken place, since the material had endured subaerial weathering and then survived several years in contact with dilute lake waters before finally becoming buried. On the other hand, he recognised the mobility of some elements (e.g. Fe and Mn) under reducing conditions. Nodules of vivianite which he observed were deemed secondary features brought about by migration of Fe and P into a precipitation centre. These theories have been applied in many subsequent lake sediment studies and may often hold in the case of oligotrophic lakes. However, it has been found that the 'record of changing soil composition of the watershed' may be apparent rather than real (Dearing, 1991).

The 1960's saw other groups building up the data base on lake sediment geochemistry. In N. America, the Minnesota group in particular were responsible for a wide body of publications between the mid 1960's and mid-1970's (Swain, 1966; Gorham et. al., 1974; Dean and Gorham, 1976). Relationships between bottom sediments and lake type were found and explained. In Scandinavia, Digerfeldt pioneered the concept of lake level reconstructions from multi-core sediment records during the late 1960's (Digerfeldt, 1966).

The 1970's were associated with the application of significant technological improvements both in coring and geochemical analysis. It became possible to carry out routine multi-element analysis on relatively large numbers of samples. Major new areas of the world received investigation with the recovery of long records, particularly East Africa (Degens et. al., 1973), Australia (Kershaw, 1978) and South America (Lewis and Weibezahn, 1981). In Switzerland a series of studies on Greifensee and other lakes provided information on the processes of freshwater carbonate formation and lake sediment diagenesis. Groups in the U.S. and Canada improved our understanding of other diagenetic minerals such as vivianite, siderite and pyrite.

A celebrated 200 metre long record was recovered from Lake Biwa in Japan by wire-line coring rig. Many geochemical and other kinds of measurements were made on the Biwa sediment record. This included the application of modern techniques such as AA, INAA, ICP and XRF. The vast amount of data collected was presented in a series of reports (e.g. Horie, 1972-81) which describe the techniques and results, but often suffer from weak interpretation or discussion in relating the sediment signatures to environmental change.

Organic geochemical investigations also increased significantly during this decade with new information emerging from compounds such as pigments and lipids (Sanger and Gorham, 1972; Cranwell, 1973). These improved investigations led to a large number of new facts and relationships and the publication of a new generation of texts (Wetzel, 1975; Lerman, 1978; Matter and Tucker, 1978).

Towards the end of the 1970's and into the 1980's more theory building took place (Oldfield, 1977; Binford et. al., 1983; Håkanson and Jansson 1983; Haworth and Lund, 1984; Stumm, 1985). Relationships between lake, catchment and driving forces (climate change, hydrology, soil and man) were reviewed more critically (Dearing and Foster, 1986). New programmes of work led to the combined multidisciplinary investigation of groups of lakes in Europe and N. America, including the EEC funded examination of maar lakes. Lake sediments were looked at in relation to evidence for geomorphological changes in the catchment (Flower and Foster, 1987) and the horizontal distribution of sediment chemistry was mapped in an individual lake (Hilton and Gibbs, 1984). More multiple core studies were carried out after Digerfeldt's pionerring efforts and sometimes revealed profound information concerning the differences in sediment accumulations between the deep and shallow water zones (Anderson, 1990; Engstrom and Swain., 1986). Workers such as Rippey (1982) attempted to make closer links between lake sediments and climatic parameters such as rainfall. At the end of the decade a new 'Journal of Paleolimnology' emerged.

The early 1990's have seen intensified efforts to improve our theoretical base for interpretation through studying well behaved systems and using laboratory modelling. A plea was made for broader cooperation between palaeolimnologists and 'neolimnologists' to meet these new challenges (Smol, 1991). There have been greater attempts to integrate long records with well known evidence for climatic change. An excellent example of this is the correlation of the record from Lake Lugano with Late Quaternary events such as the Younger Dryas and Holocene subdivisions (Niessen and Kelts, 1989). Most recently Kerry Kelts has attempted to establish a data base with the aim of correlating pronounced climatic changes from a global network of lake records (Kelts, 1993). Efforts have also intensified towards reconstructing lake level fluctuations as a source of regional climatic change (Harrison et. al., 1991; Stine and Stine, 1990). As this is taking place, new and exciting records are being recovered from crater lakes (e.g. Sacred Lake in Kenya -Perrot, unpubl. work) and from large lakes such as Lake Baikal. In small lakes with calcareous varved sediments it now seems possible to answer important questions concerning the timing of the Younger Dryas and the extent of the late-glacial radiocarbon plateau. For example, records bearing combined sidereal and ^{14}C timescales together with oxygen isotope curves, reflecting local temperature changes, may be recovered from some sites (Lotter, 1991a; 1991b).

Long lacustrine sediment records

Sites containing long records of lacustrine sedimentation (>20,000 years) are unusual and where such sites occur there may be considerable logistical difficulties in recovering long core profiles over a body of water. Long records occur in two main settings: large tectonic depression lakes and volcanic crater lakes. The former includes sites such as Lake Biwa in Japan where a continuous sediment record of around the last 2 million years has been recovered (Meyers et. al., 1993; Horie, 1984). It also includes other large lakes such as Tanganyika and Malawi in Africa and Baikal in Russia where records extending back to the Tertiary probably exist, but have not yet been cored (Frostick et. al., 1986). The relatively small crater lake sites occur in many parts of the world which have experienced volcanic activity. Lakes of this type have been studied in areas such as cental America, the western United States, west and eastern Africa, Australasia, the Middle East and Europe. These lakes have an average lifetime of several hundred thousand years and so extant lakes will probably be associated with volcanism during the last 1 M.a. In addition, settings containing long records normally occur outside areas that experienced ice activity during the last glaciation (i.e. they are constrained to the low and middle latitudes). At higher latitudes older sediments would tend to suffer obliteration by the processes of ice denudation or at best provide discontinuous time windows (e.g. Sejrup, 1987).

EUROMAARS

The EEC supported 'EUROMAARS' programme was established with the aim of recovering long, continuous continental sequences from information recorded in the sediment infill of carefully selected maar-type lakes in western Europe. From this it was hoped to examine the relationship between the climatic oscillations recorded over the last million years in marine cores and the climatic cycles apparent in a more discontinuous fashion across many disseminated continental sequences.

EUROMAARS followed on from the mid-1980's 'GEOMAARS' programme which had been concerned with similar subject matter on a shorter timescale (e.g. Documents du CERLAT, 1991). Valuable experience had been gained by the same group of workers in this earlier project, and this was utilised in selecting the most promising sites to be drilled for EUROMAARS.

Advantages of maar lakes as sources of proxy climatic data

1) Maar lakes are characterised by their persistence and stability over suitably long time scales (i.e. $>10^5$ years)

2) Sedimentation is regular due to the absence of major in- and outflows in an always modest catchment area

3) The depositional sequences that accumulate are particularly suitable for recording environmental conditions in the region around the lake.

Maar formation and evolution

The formation of a maar occurs by phreatomagmatic explosive activity excavating a crater in the surrounding bedrock (Lorenz, 1973; Ollier, 1967). Due to the necessary presence of groundwater involved in the formation mechanism, it is common for the water table to be at a height which causes a water body or lake to subsequently appear in the basin. Initial sedimentation may involve coarse detrital inwashing (Büchel and Lorenz, 1993) and alluvial fans or mass movement processes. However, after this early domination by physical sedimentation the crater slopes will normally become stabilised (with vegetation) and a more steady and subdued sedimentation ensue. Eventually the lake basin is likely to be infilled, albeit on a long enough time scale to be of interest. This may be characterised by an organic-rich mire which will eventually be succeeded by dry land. At this stage the maar has become 'fossilised' and will no longer provide a contemporary sediment record. Such maars have been recognised by trained geomorphologists, such as Jörg Negendank, and provide time windows into earlier periods (e.g. the Tertiary). However, the main interest of EUROMAARS has been with extant lake sites and records extending back continuously from the present day.

Maar lakes in Europe

In western Europe maar lakes are found in the Eifel region of Germany, in the Velay area of the Massif Central and in central and southern Italy. All three locations have received attention from the EUROMAARS and GEOMAARS programmes.

Previous studies concerning long lacustrine records from Italy

Table 1.1. shows published work on other lake sediment records from Italy. These sites have **mainly** been studied for their pollen records, although in some cases geochemical and sedimentological data have been investigated.

Site	Age	Authors
Lago di Martignano	11,000 years	Kelly and Huntley (1991)
Valle di Castiglione	250,000 years	Narcisi et. al. (1992), Follieri et. al. (1988)
Lago Vico	138,000 years	Francus et. al. (1993), Frank(1969)
Lago Monterosi	26,000 years	Hutchinson (1970)
Valle di Baccano	>10,000 years	Bonatti (1963)
Lagaccione	100,000 years	Follieri et. al. (1993)
Stracciacappa	60,000 years	Follieri et. al. (1993)
Prato Spilla	12,500 years	Lowe (1992)
Lagdei	15,000 years	Bertoldi (1980)
Lago di Ganna	14,200 years	Schneider and Tobolski (1983)
Canolo Nuovo	40,000 years	Grüger (1977)

Table 1.1. Long sediment records from Italian lakes and related enviroments.

The first seven sites are maars situated within 60km of Rome while the next two are in the northern Apennines. Lago di Ganna lies further north in the Varese region on the southern flanks of the Alps. The Canolo Nuovo deposit lies to the south of Monticchio in Calabria. Other Italian lakes have been studied, although the work appears to be concerned with present limnology and sediment records on historic time scales.

Aims and methodology of this project

It is the aim of this project to apply modern and traditional geochemical techniques in a comprehensive study of the sediment record obtained from Lago Grande di Monticchio (see Chap. 2) under the EUROMAARS programme. It is possible that the material collected from Lago Grande covers the last 200,000 years (almost continuously), in which case this work would represent an unusually detailed investigation of the chemical stratigraphy from such a long sequence. It is hoped to extract as much information as possible concerning palaeoenvironmental conditions, and particularly how the last (Eemian) interglacial may have compared to the present. Parallel studies in palynology, sedimentology and tephrochronology will aid the overall palaeoenvironmental reconstruction for this site. The results will help improve our understanding of southern Europe's late Quaternary history. Attempts can then be made to integrate this data with information currently available from the ocean and ice-core records.

CHAPTER 2

THE SETTING OF LAGO GRANDE DI MONTICCHIO

Location

Two small maar lakes, collectively known as Laghi di Monticchio, are situated in a caldera of the Monte Vulture volcanic massif, lying within the Basilicata province of southern Italy (15°36'E, 40°56'N). Lago Grande lies at an altitude of 656 metres above sea level and is subcircular in outline with a maximum diameter of 0.8km (Fig. 2.1.). It is separated from the smaller Lago Piccolo by a 5 metre bar or terrace. The site lies approximately 120km east of Naples and 7km west of the nearest town, Rionero-in-Vulture. Monte Vulture, at 1326 metres above sea level, forms the highest point in the nearby area.

Regional geology

The Vulture complex lies above a sequence of sedimentary rocks of late Triassic to Tertiary age which form the southern Apennines (Fiore et. al., 1986; Stanley and Wezel, 1985). Monte Vulture represents one of a chain of volcanic centres which developed around 1 million years ago during a phase of Quaternary crustal extension (Locardi, 1985). These volcanic centres extend from Vulture in the southeast to beyond Rome in the northwest and are characterised by perpotassic eruption products. Renewed extensional phases during the mid-Quaternary produced further volcanic centres such as Campi Flegrei which formed around 300,000 years ago (Locardi, 1985).

The Vulture volcanic complex has been studied both in terms of its geomorphological evolution and its petrographic and geochemical features. Guest et. al. (1988) provide a detailed account of the development of the complex which included an initial basal stage and a major cone building period. In the final stage, a caldera formed on the western flanks of the volcano (probably by gravitational caldera collapse) and the Laghi di Monticchio subsequently formed within this caldera by phreatomagmatic eruption.

The petrographic and geochemical aspects of the Vulture system are described in a number of papers, including Caggianelli et. al. (1990) and de Fino et. al. (1986). The bulk of the sequence is composed of foiditic and tephritic pyroclastics (fall, flow and surge deposits) with interbedded lava flows. These rocks are similar in overall chemistry to the potassic series rocks of the Roman Province, although potassium itself is a less dominant component (Caggianelli et. al., 1990). The Vulture series is also noted for its peculiar enrichments in Na, Ca, Cl, S and P. These have been tentatively attributed to the interaction of magma with aqueous solutions rich in Ca, SO_4^{2-} and NaCl, which might be related to Miocene or Mesozoic evaporitic sediments 'underlying the volcano' (de Fino et. al., 1986).

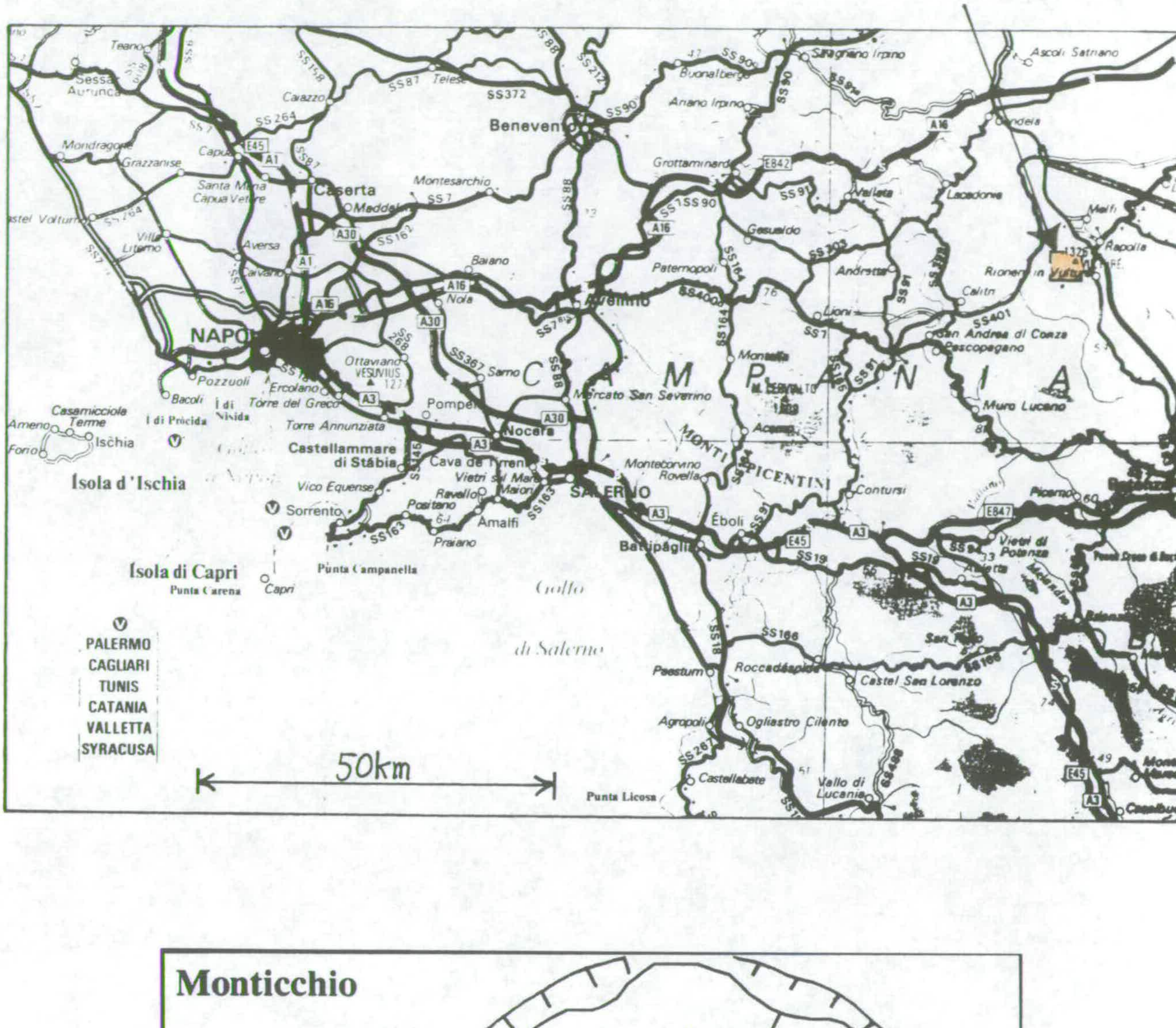


Fig. 2.1. Location of Lago Grande di Monticchio (above) and area of lakes enlarged (below)

For reference, two rocks from the Vulture sequence were collected during the coring trip and later analysed chemically and mineralogically (see Appendix 1). These samples are from outside the immediate catchment area, but within the main volcanic sequence and are believed to be similar to the rocks in the Monticchio catchment. Their composition is shown below (Table 2.1.).

major elements (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
VUL2	48.20	18.27	8.24	3.43	9.41	6.68	1.46	1.00	0.18	0.83
VUL4	44.82	17.70	8.83	4.80	11.10	4.23	4.40	1.18	0.18	0.94

	CO_2	N	SO_3	Total
VUL2	0.14	0.05	1.00	98.89
VUL4	-----	0.07	0.32	98.56

trace elements (ppm)

	Cl	Sr	Ba	V	La	Ce	Nd	Cr	Ni	Cu
VUL2	5892.2	2973.3	2174.8	211.6	285.8	484.1	170.5	13.4	11.7	71.6
VUL4	3660.9	2409.5	2343.7	269.2	212.8	382.3	143.0	40.9	17.2	87.1

	Zn	Pb	Th	U	Rb	Y	Zr	I	Br	Mo
VUL2	105.1	100.3	87.8	22.9	117.5	56.9	552.4	---	9.8	4.5
VUL4	103.0	59.5	53.8	16.7	142.2	47.6	376.4	---	5.4	3.4

Table 2.1. Composition of Vulture rocks

The data shown are comparable to results described by de Fino et. al. (1986). It can be seen that the samples contain significant enrichments in volatile elements: 0.05wt% N, 0.36-0.58wt% Cl and 0.3-1.0wt% SO_3. These elements are probably hosted by a haüyne-sodalite phase (identified by XRD) and perhaps by the glassy groundmass. In thin section, the rocks were observed to contain mainly clinopyroxene phenocrysts with some haüyne, plagioclase, corroded dark mica and apatite. The groundmass was microcrystalline to glassy and difficult to identify in further detail. It has been noted in other sudies that the feldspathoid minerals and glass of the Vulture rocks frequently exhibit deep alteration to zeolites, analcite and argillaceous material (de Fino et. al., 1986).

Age of Monticchio and the Vulture sequence

Formation of the lavas and pyroclastic rocks is believed to have begun around 1 million years B.P. (La Volpe et. al., 1984). The main cone building phase has been bracketed between 830,000 and 500,000 years B.P. (Guest et. al., 1988; de Fino et. al., 1986; Capaldi et. al., 1985). Recently Laurenzi et. al. (1993) have presented a single date of 130,000 years which they associate with the formation of the Monticchio lakes. The authors advised that this date should be treated with caution and further information is awaited concerning this work. Therefore, the date of maar formation is not yet well constrained. From the Watts (1985) palynological work on an earlier sediment core, it is thought that the sediment record in the lake covers at least 40,000 years. At present it may be assumed that Monticchio formed somewhere between 40,000 and 500,000 years B.P.

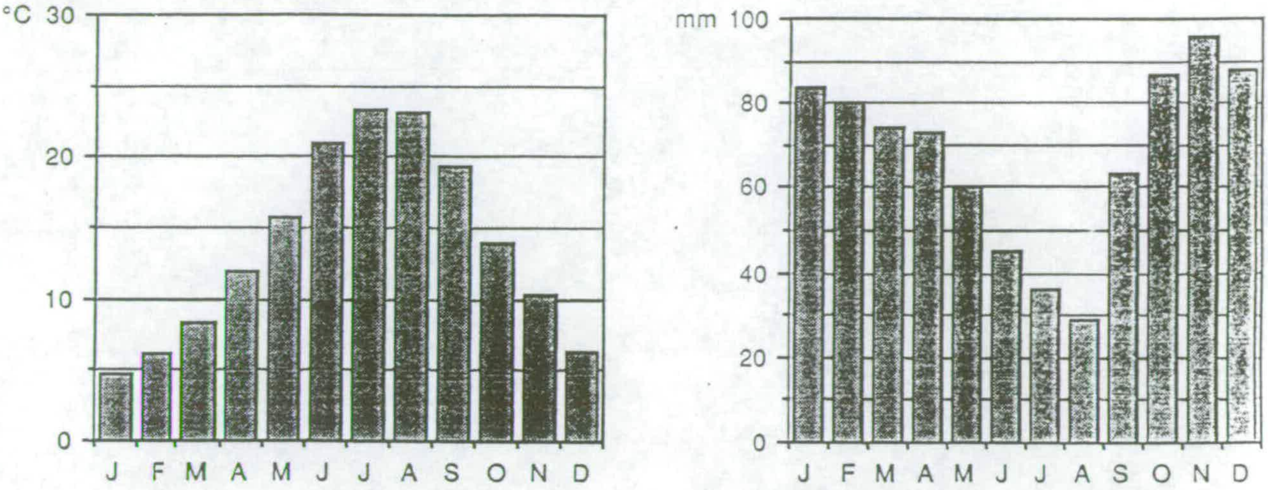
Obviously, the maar formation age provides an upper limit on the oldest sediments that could have accumulated in the lake. From the September 1990 coring work, it seems that a borehole somewhat longer than 51 metres would be required before the solid bedrock underlying the lake is encountered. Unfortunately, seismic investigations ran into the problem of high gas content in the sediments and cannot penetrate to anywhere near the bottom of sequence (Stefanon, 1993). This age question may either be resolved from a longer sediment core or from further work on the surrounding pyroclastic sequences. The former is made difficult by the problems of dating sediments outside the 40,000 year range and the latter made difficult by the poor exposure in and around the catchment.

Climate

Temperature and rainfall data from a weather station at Monticchio are shown in Fig. 2.2. The site experiences a Mediterranean climate which is probably moderated to some degree by its elevation. The characteristic summer drought is not particularly strong here with rainfall during June to September remaining above 30mm per month. The summer is warm, but not intensely hot. Winter is cool and experiences moderately high rainfall. Wind speed data is not shown, but it is thought that the steep crater walls shelter Monticchio from much of the effects of wind. During fieldwork the lake was always observed to be calm and did not display signs of wave movement.

Although the Vulture region is elevated, it is unlikely that Lago Grande was affected by the presence of ice during glacial times because of its southerly location. It would appear that only the Alps and a few areas above 2000 metres altitude in peninsula Italy experienced ice cover during the last glacial maximum (Fig. 2.2.).

Station: Monticchio - 652 m a.s.l.



Period of observation: 1930 - 1973
Number of years: 31
Mean annual temperature: 13.7 °C

Period of observation: 1920 - 1973
Number of years: 50
Mean annual precipitation: 815 mm
Rainy days: 87

Fig. 2.2. Temperature and rainfall data for Monticchio (above) and maximum extent of ice cover during the last glacial maximum (below) from West (1977)

From the palynological record at this site and others (Watts, 1985) it is believed that the region had a cool steppe vegetation and climatic regime during the glacial period. This probably comprised slightly cooler summers and considerably colder winters. Also, there was probably a strong moisture deficit during the summer growing season, with most rainfall occurring during winter. This regime may have present day analogues in Tibet and in the prairie regions of N. Dakota and Alberta (B. Huntley, pers. comm.).

Basic catchment and limnological features

Lago Grande has a present surface area of 0.4km^2 and an approximate catchment area of 2.4km^2. Therefore the ratio of catchment to lake area is 6 and this relatively low value would predict a lake system dominated by slope and surface transport processes (Dearing and Foster, 1993). This seems to be the case since fluvial activity is at present negligible. A number of small dry channels do exist in the catchment, but these may only operate under high rainfall events. The small ratio of catchment to lake area would also predict a low rate of clastic sediment accumulation in the lake basin, but the exact magnitude of clastic influx will depend on the degree to which the catchment topography is being lowered by denudation (Dearing and Foster, 1993). If it is assumed that the lake covered a present 5 metre marginal terrace zone prior to the 11th century (see later), then the catchment/lake surface area would be even lower (perhaps <3).

Lago Grande has a maximum depth of 34 metres, but **much** of the lake is a shallow shelf sloping gently from the shoreline towards 12 metres depth (Fig. 2.3.). This asymmetric profile contrasts with the more simple cauldron shape usually encountered in maars. For example, in Lac du Bouchet the lake floor slopes steeply away from the shoreline to an extensive deep basin area (Creer, 1991). It is thought that the shallow shelf area of Monticchio which is <12 metres in depth reflects a level of sediment infill that has reached a mature stage. The lake would be expected to evolve into a swamp or terrestrial environment with continued sediment accretion. The deep pit area (Fig. 2.3.) may represent a relict vent feature in the original basin shape which has not been evened by sediment infill or focusing. Sonar investigations detected the presence of vertical 'cliffs' of hard material (possibly lava) in the steep slopes leading to the deep basin (Hansen, 1993). It is possible that the vent feature may represent the site of a secondary phreatomagmatic eruption during the middle or later history of the lake. On the other hand it may be a more contemporary structure resulting from a focus of volcanic gas emanation (B. Huntley, pers. comm.). The possibility of active CO_2 degassing from the Monticchio site is currently being investigated and preliminary measurements suggest that a net volume of gas is emanating from the lake.

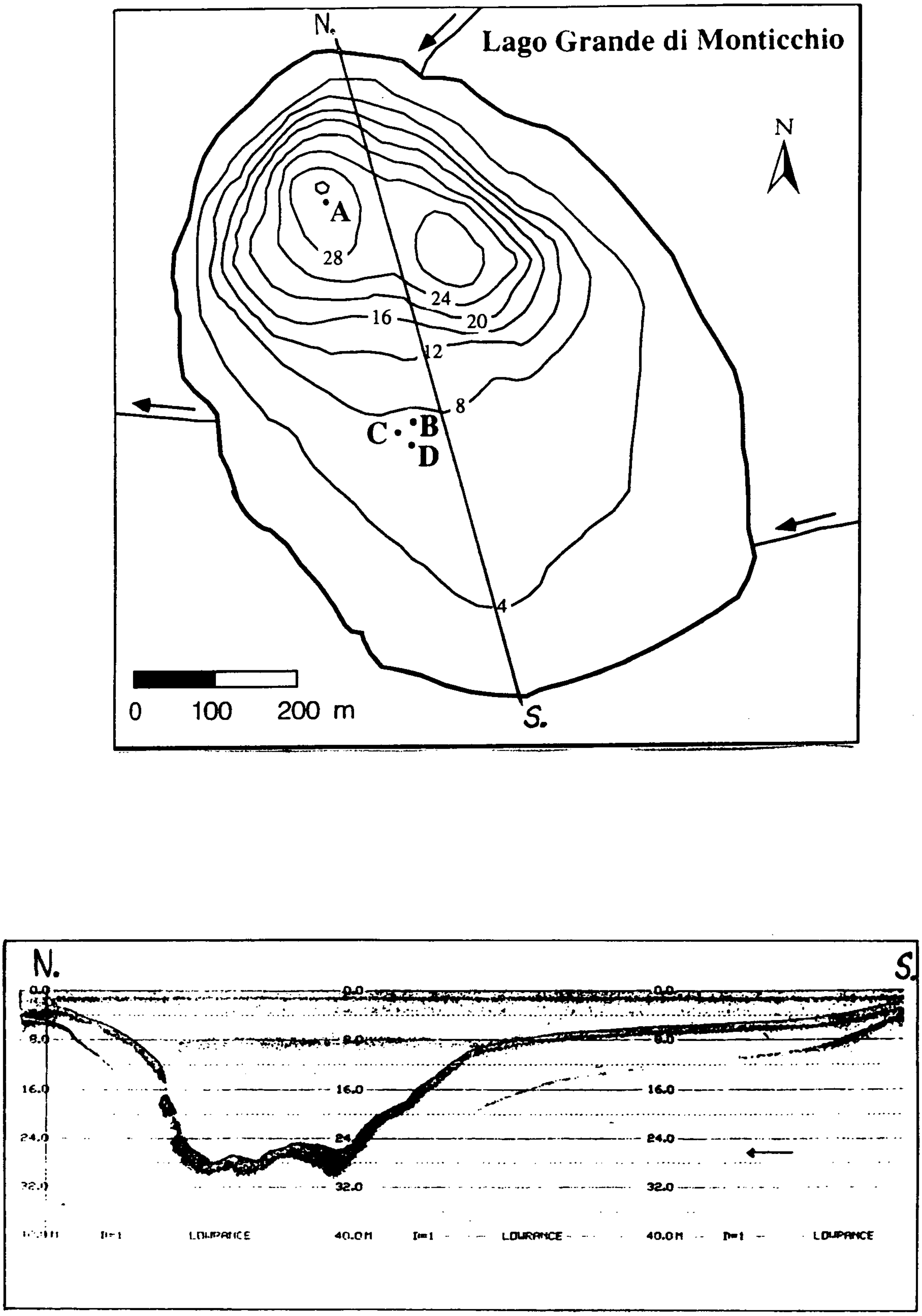


Fig. 2.3. Core sites during 1990 fieldwork and lake bathymetry (from Hansen, 1993)

Plate 2. Lago Grande in the distance viewed from the S. Michele monastery (above), and piston coring operations on the raft (below).

It is believed that the lake is spring fed and thus regulated by the local groundwater system (B. Narcisi, unpubl. work). This will probably be augmented by direct rainfall and surface runoff during wet periods. It might be expected that the Mediterranean summer drought would cause the lake level to lower (e.g. Hutchinson, 1970). This effect is estimated to be <70cm between spring and summer (B. Huntley, pers. comm.) and is not a dramatic seasonal change. In comparison, other Mediterranean lakes under different hydrological regimes have recorded fluctuations greater than 8 metres over short time periods (Flower and Foster, 1992). It is probable that the groundwater reserves buffer any seasonal or decadal switches due to climate. Therefore major lake level changes at the site are thought to require long term climatic changes or permanent alterations to the tectonic-hydrological system.

The lake is presently eutrophic to polytrophic (Zolitschka and Negendank, in prep.). This is illustrated by the high densities of macrophytes in the shelf zone (particularly in the shallowest 4 metres of water) and by the green water colour reflecting surface algal productivity. Gelatinous films of blue-green algae are also observed and are typical indicators of anthropogenic pollution. Limited stocks of fish appear to exist in the lake, although these may not thrive under the conditions of high productivity.

According to high amplification rate sonar measurements (Hansen, 1993) there is probably a 'sparse' thermocline present at around 10 metres depth, at least during the summer period. This implies that the shelf site where cores B to E were taken (see later) currently lies in the epilimnion zone. Further sonar results suggest an absence of fish shoals below 4 metres depth which might be an indication of oxygen depletion. It is not certain whether Monticchio is characterised by permanent stratification or seasonal stratification with subsequent overturn during the winter. This situation may well have changed over recent decades due to human disturbance of the lake system. The low wind action in the basin and its small surface area are thought to allow only minimum wave activity. This situation is conducive to the development of stratification or chemical gradients in the waters. Since wave action is a major driving force for redeposition processes (Hilton et. al., 1986) it is thought that sediment focusing may not be an important influence on the Monticchio environment.

The lakes are surrounded on three sides by a steep crater whose slopes support a stable cover of mainly beech and oak. High deciduous forest of this type is believed to represent the natural vegetation for this part of the Apennines (Watts, 1985). The fourth side opens into a valley which is at present dry. The dry stream here forms a theoretical inflow at present. However, if the lake level was around 50 metres higher than at present, it would provide a major outlet towards the Ofanto valley in the west. Possible terraces are present on the flanks of this valley and it may be speculated as to whether the lake actually ran into this channel at previous times. This would seem to require a dramatic change in hydrological configuration to operate.

The soils in the catchment zone are expected to represent the main source of clastic material to the lake sediments, having been derived from underlying tephritic and foiditic rocks by weathering. As yet the soils have not been sampled or studied, although they appear at first sight to be well-established and reasonably thick. According to a European atlas of soils (FAO-Unesco, 1974), the Monticchio region is associated with soil type "Bea-½ad". This is an ando-eutric cambisol of coarse to medium texture, with associated orthic luvisols and vitric andosols. Such a soil is by definition of volcanic origin and may reflect characteristics of the parent rock as much as prevailing climatic regime (Duchaufour, 1982). The soil types that occur in this setting may vary from the young, base-rich and eutrophic state to the more developed humic-allophane complex state with substantial losses of bases and immobilisation of phosphorus by aluminium. Brunification (clay development in the B horizon and preservation of iron hydroxides) may also influence the soils developed here. This will reflect on the prevailing Mediterranean climate (Duchaufour, 1982).

A 120 metre wide terrace (Watts, 1985) approximately 5 metres above the present shoreline indicates a previously higher water level for the lake. This is thought to be connected with the foundation of a monastery (see next section). The terrace earth is known to contain diatoms which can easily be dug up below the surface (B. Zolitschka, pers. comm.). On the lower parts of the terrace a swamp of alder, willow and poplar surrounds the lake margins. The swamp grades through rich stands of rush vegetation into the shallow water areas of the lake proper. This feature provides a filter or barrier to sediments reaching the lake from the crater slopes and ensures minimal influxes of clastic material at present. However, clastic sedimentation may still have been low when the lake waters actually reached up against the foot of the crater slopes.

Seismic activity has been documented in the recent past, most notably the large 1980 earthquake that hit Campania and Basilicata (Westaway and Jackson, 1987). The devastation associated with this was still widespread during a 1982 field trip (B. Huntley, pers. comm.). This sort of activity might be expected to disrupt the surface sediment layers or temporarily increase erosion rates through tilting and shaking movements at certain times during the lake's history.

Human activities

Recent activities in the catchment such as burning of vegetation for cultivation and the input of sewage from hotels etc. were evident during 1990 fieldwork at the lake. The clearance of vegetation mainly appears to be carried out in a northwestern segment of the catchment and the rest of the catchment consists of mature woodland. Tourism is centred on weekend or day visitors from local areas. These human effects have probably led to further eutrophication of an already productive lake. Recommendations have been made that the upper few metres of organic rich sediments in Lago Grande should be removed by dredging in order to improve the potential of the lake for fishing and leisure activities (A. Stefanon, 1993). Although the present anthropogenic effects may have a marked influence on the youngest lake sediments, such effects are not thought to be of influence in the sediment record studied here because these cores do not include the uppermost 40cm (possibly >300 years) of sedimented material.

Earlier historic information documents the construction of a monastery in A.D. 1059 at San Ippolito (Fig. 2.1.). Evidence from a 5 metre terrace above the present lake level suggests that this event may have been associated with artificial drainage of the Laghi di Monticchio (Zolitschka and Negendank, in prep.). It is thought that prior to this time Lago Grande and Lago Piccolo may have been joined as a single lake with a considerably larger surface area.

Information on Roman settlement and activities has not been found specifically for the Monticchio site. However, it might be assumed that some cultural activity took place locally between say 450 B.C. and 400 A.D. Nearby Bronze Age sites have been noted at Rapolla (9km to the NE) and Melfi (10km to the NE). It is possible that cultures reflecting this level of technical development (and perhaps a later Iron Age equivalent) may have influenced the Monticchio environment, say between 4000 and 400 B.C. This would involve peoples of Greco-southern Italian origin (B. Huntley, pers. comm.). There appear to be few records of earlier human activities in this part of northern Basilicata (D. Ridgway, pers. comm.). This might, however, reflect the lack of detailed investigation that has been made.

Previous investigations

The Vulture region appears to have been studied for at least the last 30 years in connection with its volcanic features. However investigation of the sediments of Lago Grande di Monticchio may have begun with exploration by Bill Watts and Brian Huntley during the early 1980's. These workers made trips to the lake in 1982, 1984, 1986 and 1988 to collect hand-held Livingstone cores from the swampy margins. During the 1988 trip they were joined by a team from Edinburgh University and Mackereth cores were taken from deeper parts of the lake. The success of the palynological results (e.g. Watts, 1985) and the potential for other studies such as tephrochronology led the site to be included in the Euromaars 'deep drilling' programme of fieldwork during 1990.

The 1990 Coring Trip

During early September 1990, a combined team under the EUROMAARS programme recovered a series of cores covering just over 51 metres of sediment from Lago Grande di Monticchio. Operations were carried out using a modified Livingstone (piston) corer mounted on a raft. The coring equipment, largely of German design (Usinger, 1991; Livingstone, 1955), had been transported to the site by lorry at a cost of around £7000. Cores B, C and D covering the main profile were taken in the shelf zone under 6 metres depth of water (Fig. 2.3.). A shallow core (Core E) was also taken within a few metres of this location. Core A had previously been taken in the deep cauldron zone of the lake under 30 metres depth of water (Fig. 2.3.). However, coring was abandoned at this location owing to the chaotic and inpenetrable nature of the sediments. Together, Cores B/C/D/E make up a 51 metre master sequence (Fig. 2.4.) which has been used for all the studies. The top of this master sequence is nominally taken as 0cm, but in actual fact the sediment water interface is a further 40cm above this. These uppermost sediments were not collected in the piston core series because they would be too unconsolidated to recover properly.

After the cores had been recovered they were transported to Trier in Germany where they were extruded later in September. While the material was in prime condition, all core sections were photographed and described visually. It was possible to correlate individual core sections, again visually. Due to the range of studies being made (Table 2.2.), the cores had to be subsampled and material was brought back to Edinburgh for analysis (Appendix 1).

Institution	Investigations
Edinburgh University	palaeomagnetism, geochemistry and tephrochronology
Trier University	varve analysis, sedimentology
Louvain-la-Neuve	ostracods
Dublin and Durham Universities	palynology, plant macrofossils (and diatoms?)
Rome	geomorphology,tephrochronology

Table 2.2. Parallel studies undertaken on the 1990 core sequence

Basic core stratigraphy

The sequence broadly consists of laminated muds and gyttjas with occasional layers of coarser material. Sediments from Core D are illustrated in Plates 3-5. This core covers the zone between 170 and 5100cm depth and the core sections shown pass downwards from right to left and from top to bottom on each Plate.

In the upper sections a brown diatom gyttja (0-500cm) grades into black, highly organic mud (500-850cm.) The latter contains localised patches of vivianite up to 5mm in size. These upper 850cm of sediments are the most organic-rich in the profile and have a distinct pulpy or gelationous texture as well as high water contents.

Below 850cm the sequence continues with laminated pale brown or olive-grey muds. These occasionally grade into darker and presumably more organic-rich zones, but not of the same quality as the upper 850cm. Horizons rich in plant material (mostly mosses) occur locally and are up to 2cm in thickness. These are particularly noticeable between 900 and 1900cm depth. The sequence is interrupted by a relatively coarse and clastic-rich zone of silty 'turbidites' between 1900 and 2120cm. Two slump units are found at 2200cm and at 2800cm depth. Both these are over a metre in thickness. However, the bulk of the sequence is characterised visually as a series of laminated muds.

Tephra layers are found throughout and provide useful stratigraphic markers. They are of varied compositional nature and range from >20cm in thickness to microscopic horizons not readily detectable.

If the moss horizons in the record represent in situ growth this might imply a low lake level over the core site at such times. Such macrophytic plants require light penetration to photosynthesise and this would probably necessitate a maximum of 3 metres overlying water in a productive lake (Moss, 1982). However, the macrofossils may have grown in a wet environment nearer to the shoreline and be washed in as a concentrated layer (W. Watts, pers. comm.). There do not appear to be indicators in the sediment record for lake desiccation or emergence since the presence of soil or peat horizons, evaporite deposits or oxidised layers has not been observed. This suggests that the sediment record may be more or less continuous. It may be possible that the slump units or turbidites are associated with the erosive removal of packages of earlier deposited sediment, but this process is thought to account for only brief gaps in the record from this type of basin (W. Watts, pers. comm.).

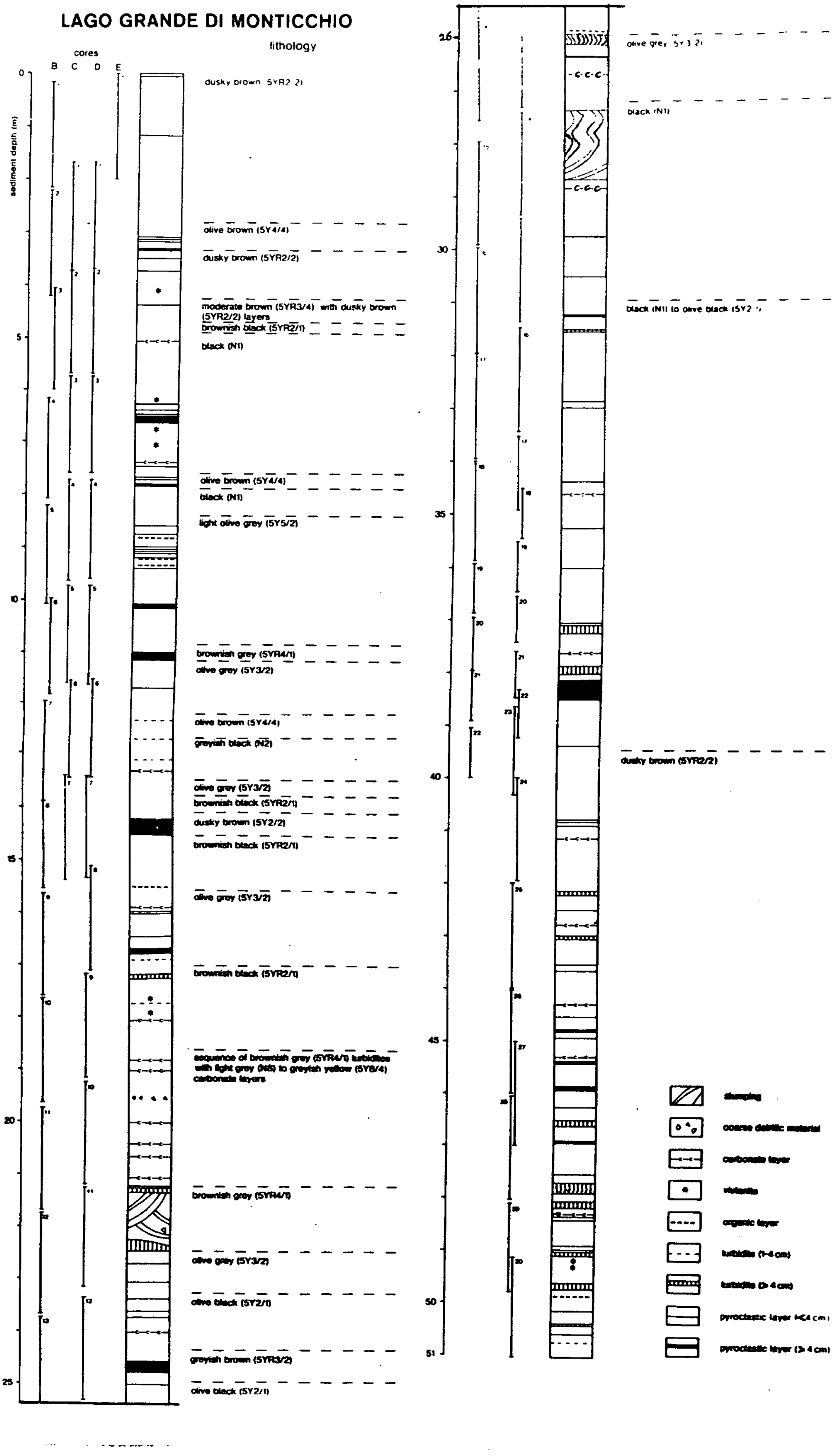


Fig. 2.4. Basic log of the 51 metre 1990 core sequence (Zolitschka, unpubl. work)

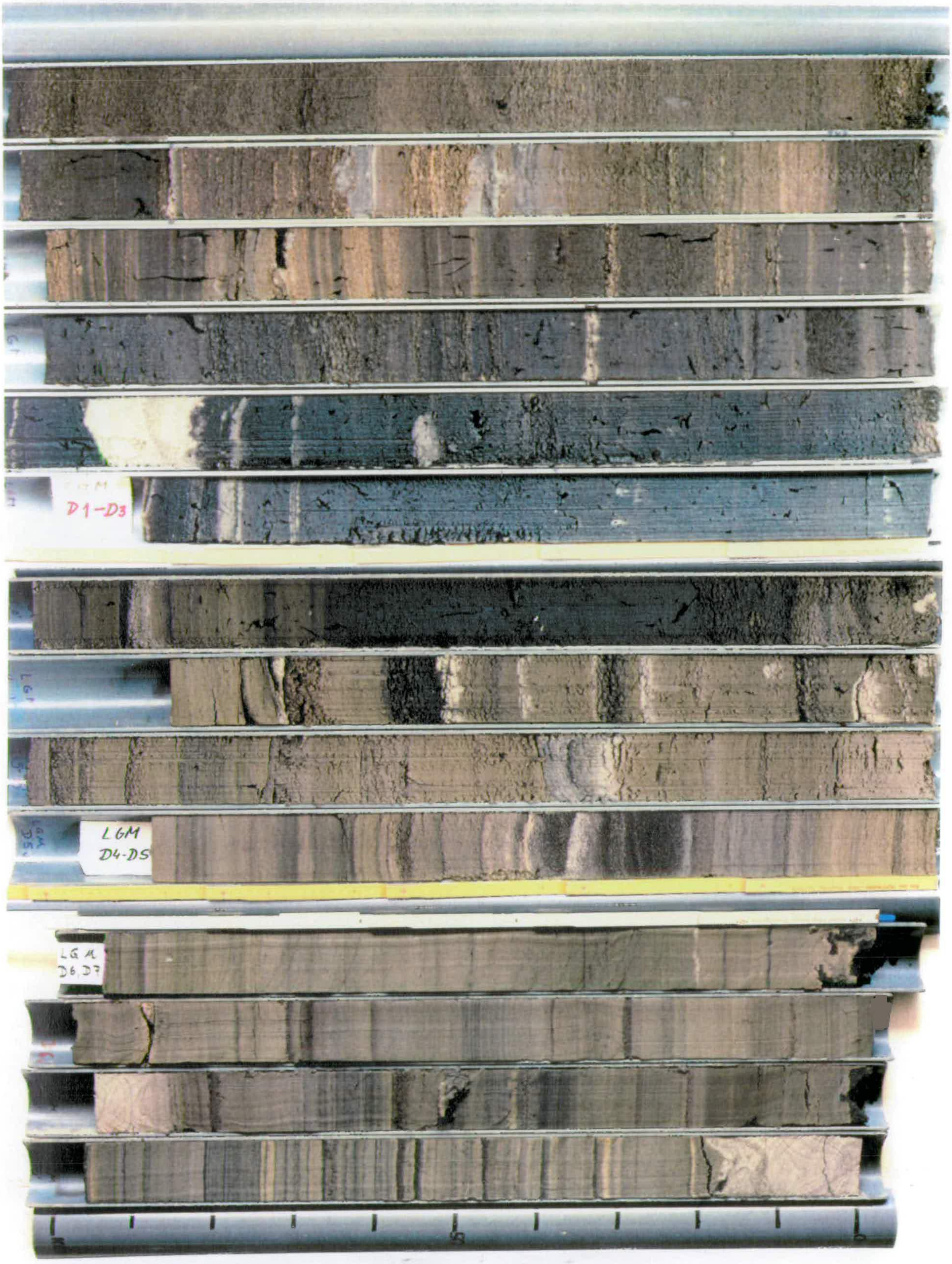


Plate 3. Core D (D1-D7)

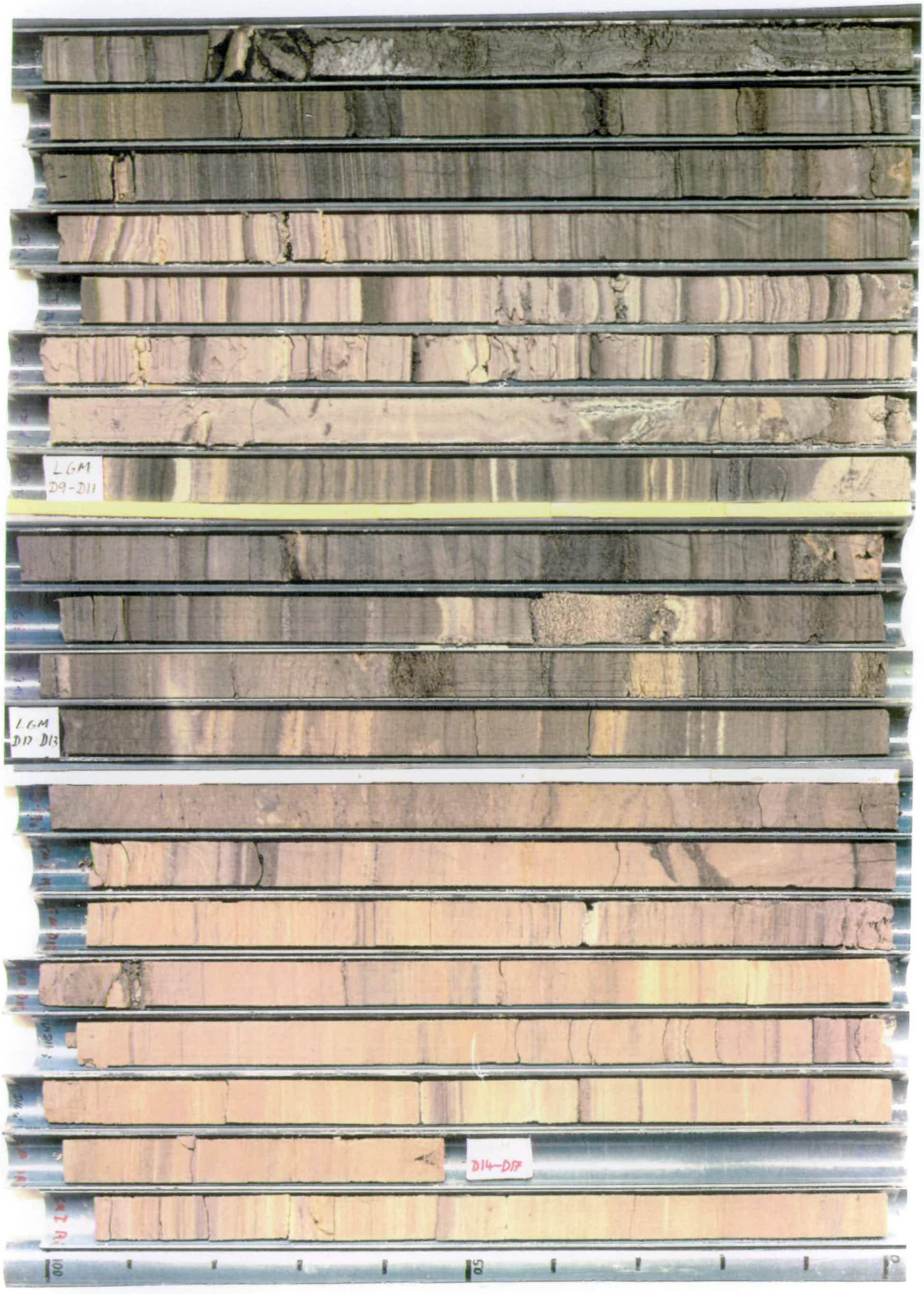


Plate 4. Core D (D8-D17)

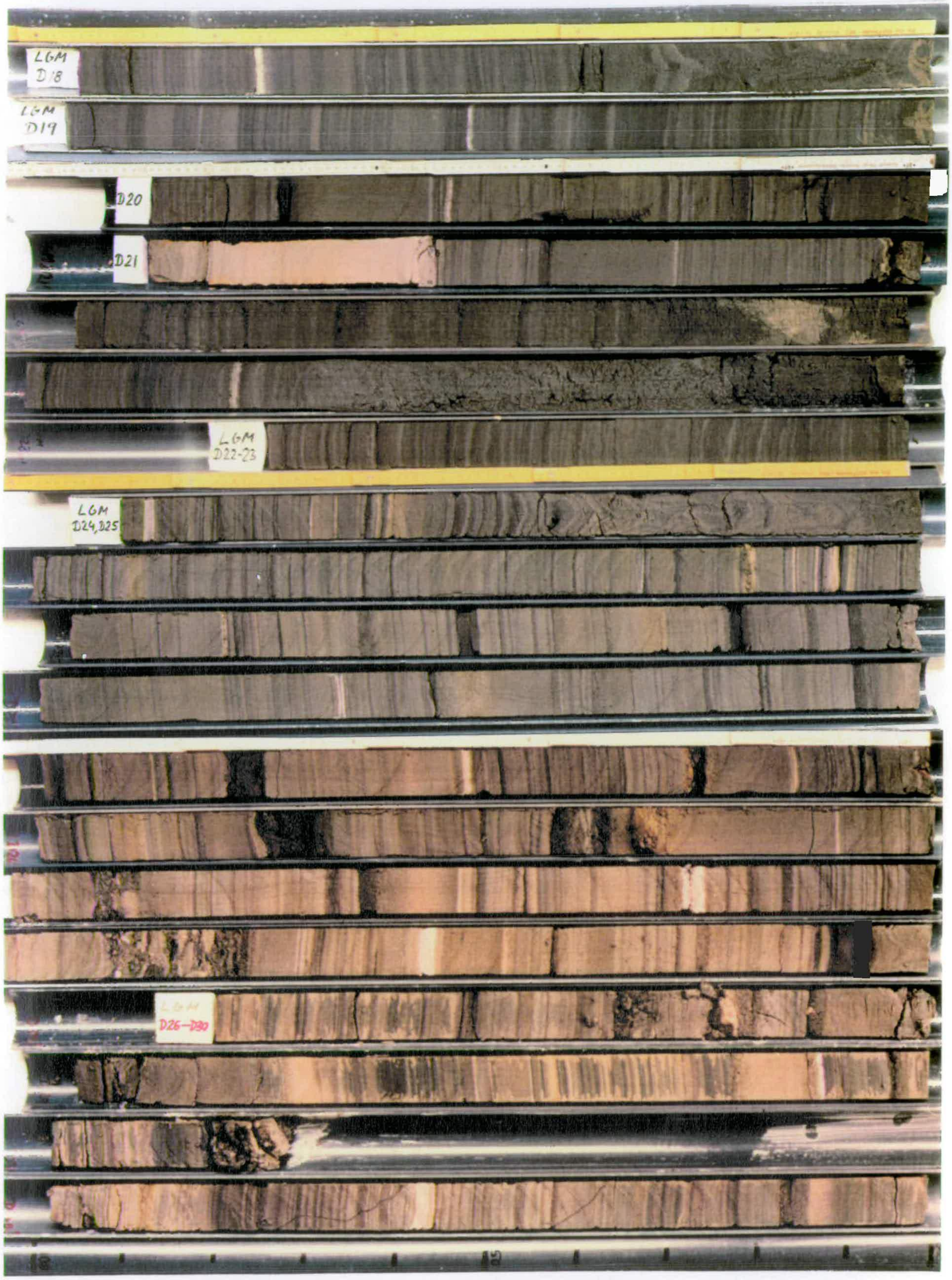


Plate 5. Core D (D18-D30)

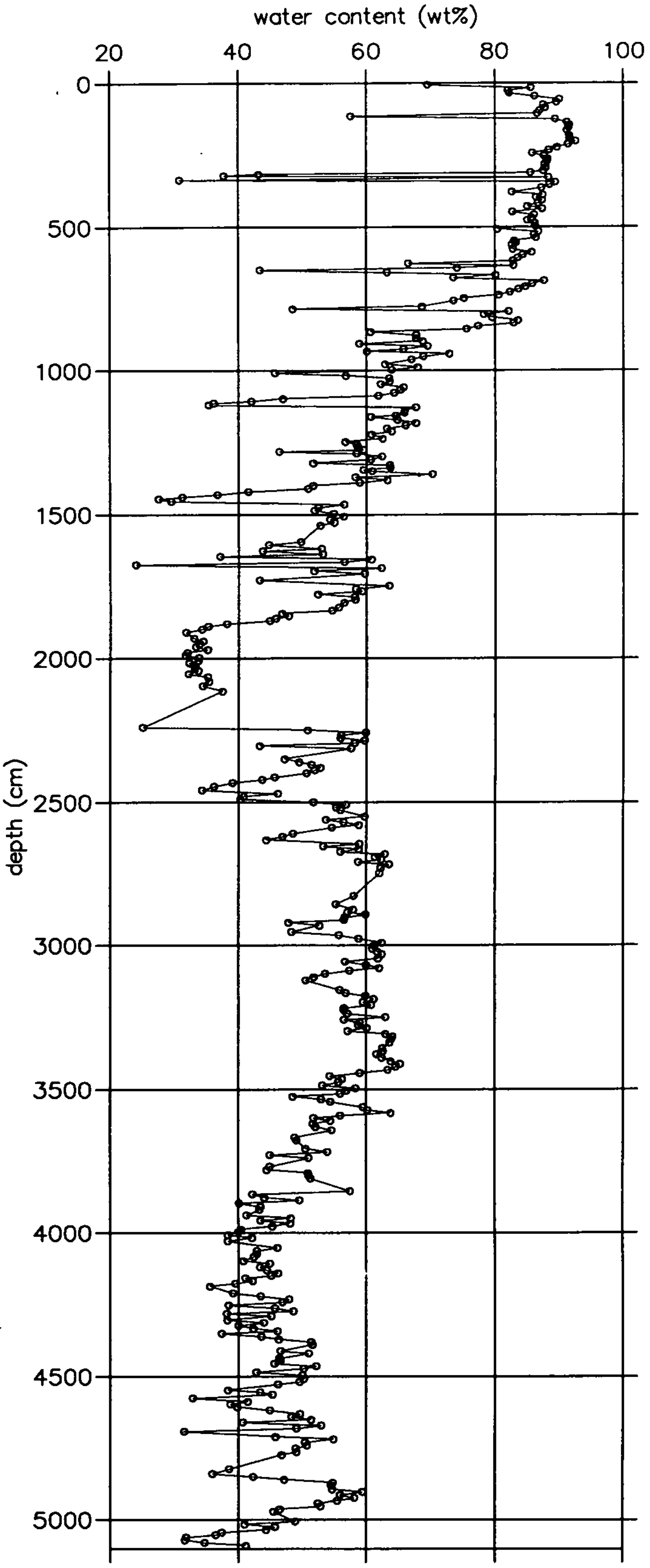


Fig. 2.5. Water content profile

Water content

A water content profile for the sequence is shown in Fig. 2.5. The upper 850cm of sediments which are highly organic are characterised by water contents of 80wt% or more. These sediments will be the least compacted in the profile and may also contain more water because of their sponge-like organic composition. The exponential decrease in water content with depth typically observed due to early sediment compaction (Foster et. al., 1990; Bengtsson and Enell, 1986) does not appear to be a feature of this upper 850cm zone. However, below 850cm the water content drops rapidly towards 60wt% and remains around or just below this value for the rest of the profile. It is believed that the relative constancy between 1000 and 5100cm indicates that further increases in compaction are slight. The variations observed may largely reflect compositional changes in the sediment and thus relative compactability. For example, the more organic rich sediments around 2700-3400cm and at 4900cm depth contain above average water contents, while the clastic dominated (and relatively coarse) sediments around 2000cm depth have unusually low water contents. As a basic starting hypothesis it is predicted that the sediments in the upper 850cm represent shorter slices of time interval per metre than the deeper sediments. This may of course be invalidated by opposing changes in the quality or quantity of sediment deposited.

CHAPTER 3

SEDIMENT GEOCHEMISTRY AND DATING OF THE MONTICCHIO SEQUENCE

LAKE SEDIMENTATION

A cartoon is presented to illustrate many of the environmental processes thought to be contributing to the sediment of a lake such as Lago Grande di Monticchio (Fig. 3.1.). In combination, these environmental processes will create the geochemistry recorded in the lake sediment record.

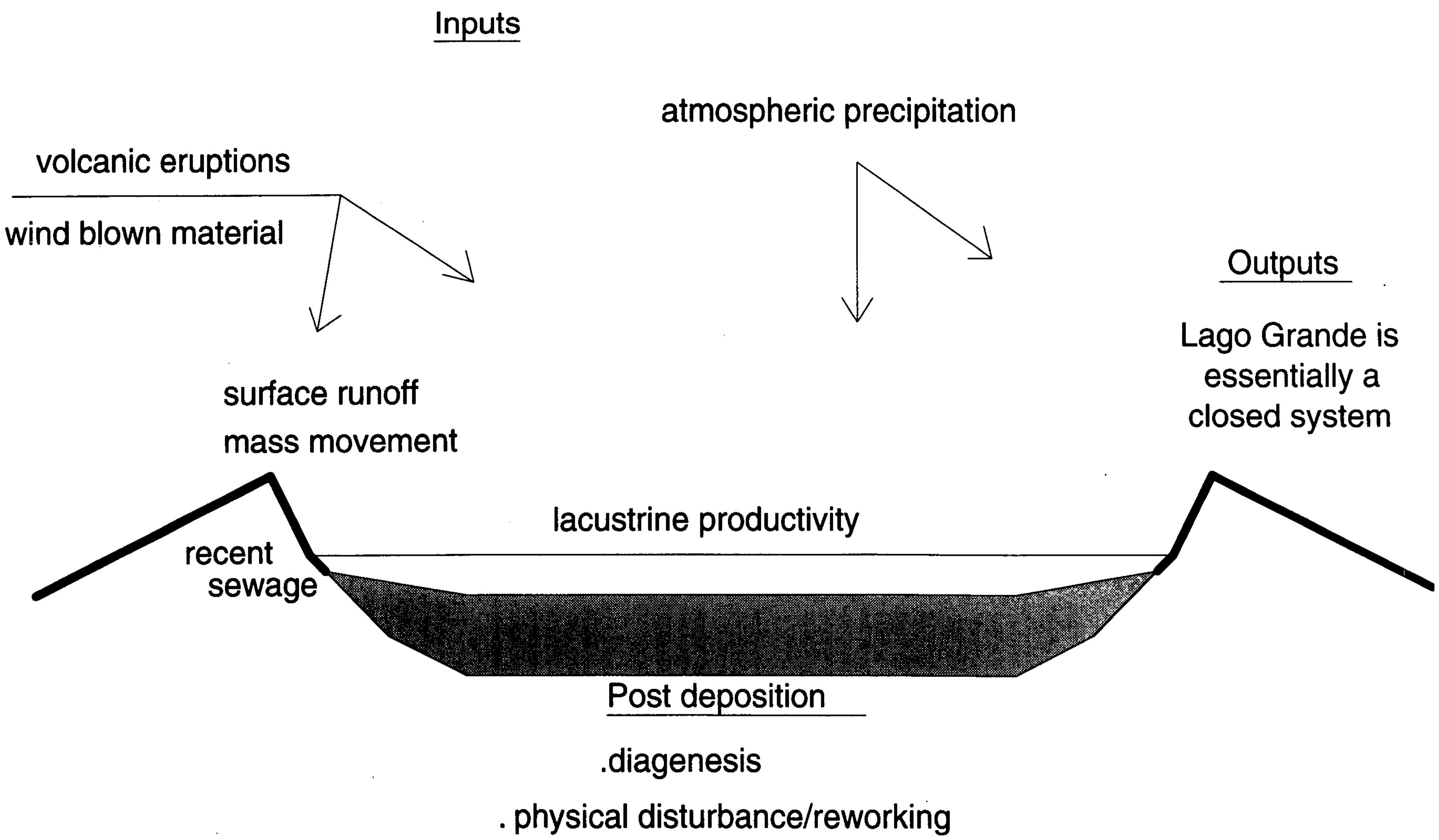
In a maar-lake setting clastic material is supplied mainly by surface runoff and mass movement, such as soil creep, within the small catchment area. At present, no streams are found draining into the lake and so fluvial inputs are thought to be unimportant. Clastic input from crater denudation will be augmented by sporadic inputs of volcanic material or tephra fallout. This is readily apparent from the numerous tephra layers preserved in the core. A more continuous input of material from further afield might occur by aeolian processes, particularly during more arid periods. Productivity within the lake (diatoms, green algae, macrophytes, ostracods, etc.) will contribute to the biogenic sedimentation together with organic matter brought in from the catchment area. These primary inputs may be affected by diagenetic processes such as the degradation of organic matter and the release/enrichment of redox sensitive and diagenetically mobile elements such as iron, manganese and certain trace metals. Also, the presence of slump units suggests that physical disturbance of the sediment takes place occasionally and this could be brought about by heavy rainfall or earthquake activity.

These environmental processes may change, and so alter the sediment geochemistry, in response to a number of primary driving forces:

1) climate
2) volcanism
3) ontogeny or evolution of the maar-lake system
4) human/anthropogenic effects

The climatic factor is of particular interest in studies of the Quaternary. It has both global and regional significance, whereas factors 3) and 4) are of more local significance. It is desirable to separate out the effects, as seen in the sedimentary record, of these primary factors in order to reconstruct the past environment as clearly as possible. The human factor is expected to influence only the most recent 5000 years or so of the record (Chap. 2), but the climatic signal may be obscured in other parts of the record by factors 2) and 3). Changes in the lake ecosystem, such as the gradual infilling of the lake basin and its succession to a

Fig. 3.1. Environmental processes contributing to the sediment geochemistry



mire, are a feature common to many lakes owing to their limited geological lifetime. This can cause sedimentation differences between lakes situated within the same climatic regime and contrasts somewhat with the deep sea environment where conditions may be uniform over large areas and stable for thousands of years. Volcanism adds a further complication not normally encountered in many lakes. It is obvious that the irregular input of volcanic material may affect the rate of sedimentation and productivity and inflict noise on underlying sedimentary climatic signals.

PALAEOLIMNOLOGY FROM THE SEDIMENT GEOCHEMISTRY

From the product of the above processes (i.e. the lake sediment record) it is necessary to work backwards using the chemical stratigraphy to deduce these environmental processes and hopefully their driving forces. The individual chemical elements in a lake sediment do not behave in complete independence, but are related through organic phases and minerals to the sedimentary processes. It is important to recognise with which phases in the mixture each element is associated in order to interpret the record well. This need to identify the origins of different chemical parameters has led to various geochemical classification schemes. Jones and Bowser (1978) suggest that the sediment components be distinguished in terms of allogenic, endogenic and authigenic sources. Each of these fractions would be expected to give information on different aspects of the lake system and help 'to elucidate the important types of interactions between lakes and sediments.' Engstrom and Wright (1984) choose to combine the endogenic materials into the authigenic fraction and thus have just two fractions. They emphasise many of the difficulties in making distinctions into such fractions. From the initial analytical results and multivariate data appraisal, it was decided in this study to group the geochemical discussion into terrigenous clastic, biological and diagenetic fractions. The terrigenous clastic fraction broadly corresponds to the allogenic fraction mentioned above. The biological fraction considers both endogenic (i.e. autochthonous) biological matter and organic matter of allogenic origin (i.e. allochthonous) in one group. The diagenetic fraction is similar to the authigenic fraction of Jones and Bowser (1978), but also incorporates chemical precipitates that might form in the water column. Although some elements are connected with more than one fraction, causing overlap, this approach was felt to be the simplest way to proceed with the discussion. The types of information that might be reconstructed from each fraction are shown in Table 3.1.

To unravel the environmental information present in the sediment geochemistry also requires an understanding in terms of geochemical processes operating in the system. Fig. 3.2. identifies many of these geochemical processes by presenting the pathways in which

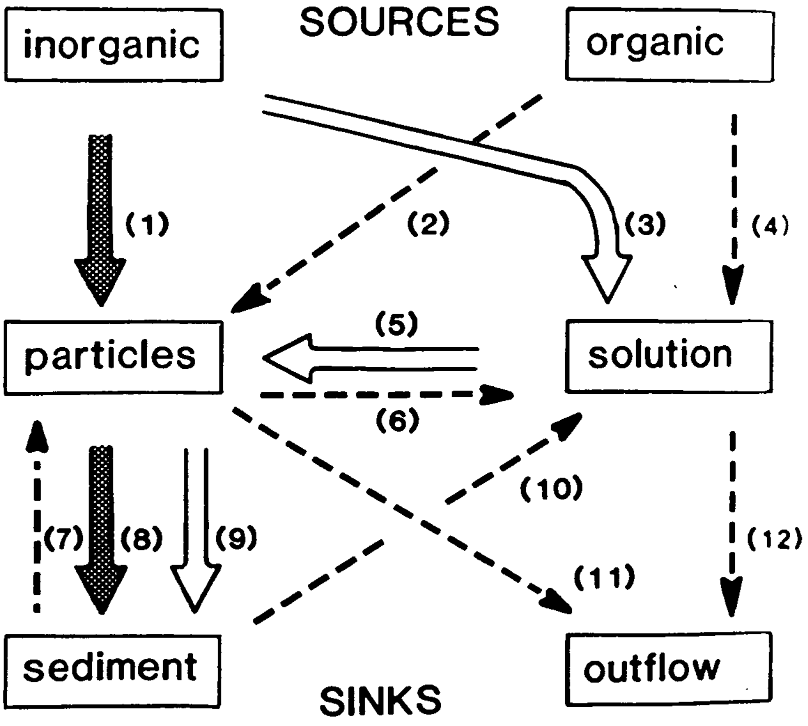


Fig. 3.2. Pathways for the transport of metals in hydrological systems (Hilton et. al. 1985)

1=mineral erosion

2=supply of detrital material

3=leaching

4=microbial decompostion

5=adsorption/coprecipitation

6=desorption/dissolution

7=resuspension

8,9=particle settling

10=redox/desorptive release

11,12=hydraulic losses

sediment fraction	information on
terrigenous clastic	catchment erosion/weathering, tephra input activity, aeolian dust transport (-climate?)
biological	lake productivity/nutrient status, catchment soil and vegetation quality (-climate?)
diagenetic	redox, pH and ionic concentrations in the sediment zone and overlying lake water

Table 3.1. Potential information available from each of the sediment fractions

chemical components can leave and enter the sediment. In the case of Monticchio it is thought that the hydraulic losses through outflow are unlikely. An additional pathway that might be included in this diagram is the diffusion into the sediments and subsequent precipitation of dissolved components. This would operate in an opposing direction to the redox/desorptive release process and might include, for example, sulphate reduction. The diagram illustrates the possibility that metals may either be transported to the sediment directly (shaded solid arrows) or reach the sediment after going through a phase in solution (open solid arrows). To differentiate between these indirect and direct pathways clearly requires a good knowledge of geochemical behaviour.

THE MEASUREMENT APPROACH

The most traditional technique for lake sediment geochemical reconstructions has involved the measurement of elemental concentrations within bulk sediment samples (Mackereth, 1966). This is the method adopted in the present study.

It might be expected that geochemical analysis of separated sediment fractions would provide for a more effective reconstruction than trying to disentangle complex information from the bulk material. However the extract approach requires much greater time and effort to carry out and a 'precise division of conceptually distinct fractions is difficult to attain' (Engstrom and Wright, 1984). It is only recently that standard procedures involving selective chemical attack (Engstrom and Wright, 1984; Bengtsson and Enell, 1986) have been proposed for lake sediments. The detail of reconstruction obtained by Heathwaite and O'Sullivan (1991) using these procedures indicates their potential effectiveness, but for the

Monticchio study a high number of sample points was favoured over this higher degree of quality. In an attempt to overcome some of the deficiencies of bulk geochemistry, use will be made of appropriate geochemical ratios to distinguish more information.

Expression of the geochemical data in raw concentration terms reflects only the relative sediment composition. It is necessary to convert concentrations to accumulation rate values (expressed in $g.cm^2.yr^{-1}$) in order to identify how net depositional rates have changed. If sediment density measurements and sedimentation rate values are known, the accumulation rate of a component, C, is calculated by:

$$C_{acc} = C_{conc} \text{ (wt\%) } * \text{ dry bulk density } (g.cm^{-3}) * \text{ linear sed'n rate } (cm.yr^{-1})$$

It would be desirable to look at how fluxes per unit area of chemical components have changed over time as an aid to deciphering the palaeoenvironment. This would enable identification of how fast processes have operated at and changed in the past. Although the dry bulk density information is available for the Monticchio record, the sediment chronology is still very uncertain and it is not possible to apply sedimentation rate values with any degree of reliability. Therefore the data cannot be converted to accumulation rates at present. It may be possible to make this calculation in the future if varve counting results and improved radiometric dates become available.

Another feature of the study of Lago Grande di Monticchio is the fact that interpretation of the sediment record is being made from a single core profile. In some lacustrine settings 'one good core' is considered to give a sufficient picture for the whole lake system. Other studies (Engstrom and Swain, 1986; Anderson, 1990) have shown that one coring location does not provide the whole story and may indeed distort the overall interpretation. The EUROMAARS team only recovered deep core material from one shelf-zone site on Monticchio after having abandoned operations in the deep cauldron part of the lake, so logistically it is only possible to carry out this study on one profile in space. It would however be interesting in future work to study core profiles from the deep part of the lake.

MULTIVARIATE ANALYSIS OF THE GEOCHEMICAL DATA: a data summary

It would be expected from the known geochemical behaviour of elements (e.g. Goldschmidt, 1954) that the 35 parameters determined on each sample would separate into various subgroups associated with the different phases contributing to the sediment. This appears to be the case if, for example, organic carbon (Fig. 4.1.) and bromine (Fig. 4.15.) are compared.

These two elements show very similar profiles and could perhaps be grouped together into an association reflecting organic matter in the sediments. To aid differentiation between possible groupings multivariate data analysis was applied. This is able to summarise the large amount of information available by reducing redundancy in the data set while retaining maximum information on how the complete data varies. It offers a more objective and efficient alternative to sitting down and comparing the 35 separate graphs visually.

The two main types of multivariate analysis are cluster analysis and ordination methods (Birks and Birks, 1980). Ordination was used in prefence to cluster analysis in this study because it is easier to deal with the large number of sample points and their representation using this technique. Also, cluster analysis imposes discrete structure on the variables and is unable to show the continuous variation (to be expected from geochemical data) within and between groupings that ordination can (Prentice, 1986). Ordination methods operate by extracting eigenvalues and eigenvectors from the original data in a matrix form (Jöreskog, 1976; Davis, 1986). Both princpial components analysis (PCA) and correspondence analysis (basic and detrended) were applied to the data set. All the samples were included for these operations.

PCA is probably the most straightforward ordination technique and is available on many computer statistical packages. At first, the data acquired from the upper 15 metres of the core was examined by this method. Ordinations were made on a correlation matrix after the data had been normalised by standard deviations. The results obtained are best displayed graphically. Fig. 3.3. shows how the two main axes of variance (principal components 1 and 2) projected onto a scatter plot divide the elements measured on samples from the upper 15 metres of the profile into fields and groupings. This is an example of R-mode analysis, i.e. investigating the similarities between the variables (chemical elements). With the information already known concerning the sedimentology and mineralogy of the core and by applying geochemical inferences (e.g. Park, 1974) a number of possible associations can be stated:

a) -the tight clustering of Corg, Br and N is related to organic matter (plants and animal soft parts)
b) -biogenic silica (bSil) represents contributions from diatom productivity and appears to be associated with S
c) -a band or arch of elements extending from Ni to Zr could represent incompletely weathered igneous minerals (eg. pyroxene), clays and heavy minerals (eg. zircon)
d) -Rb, K and Na (and to some extent Cl and Ca) may be associated with feldspars/feldspathoids, especially in tephra derived material

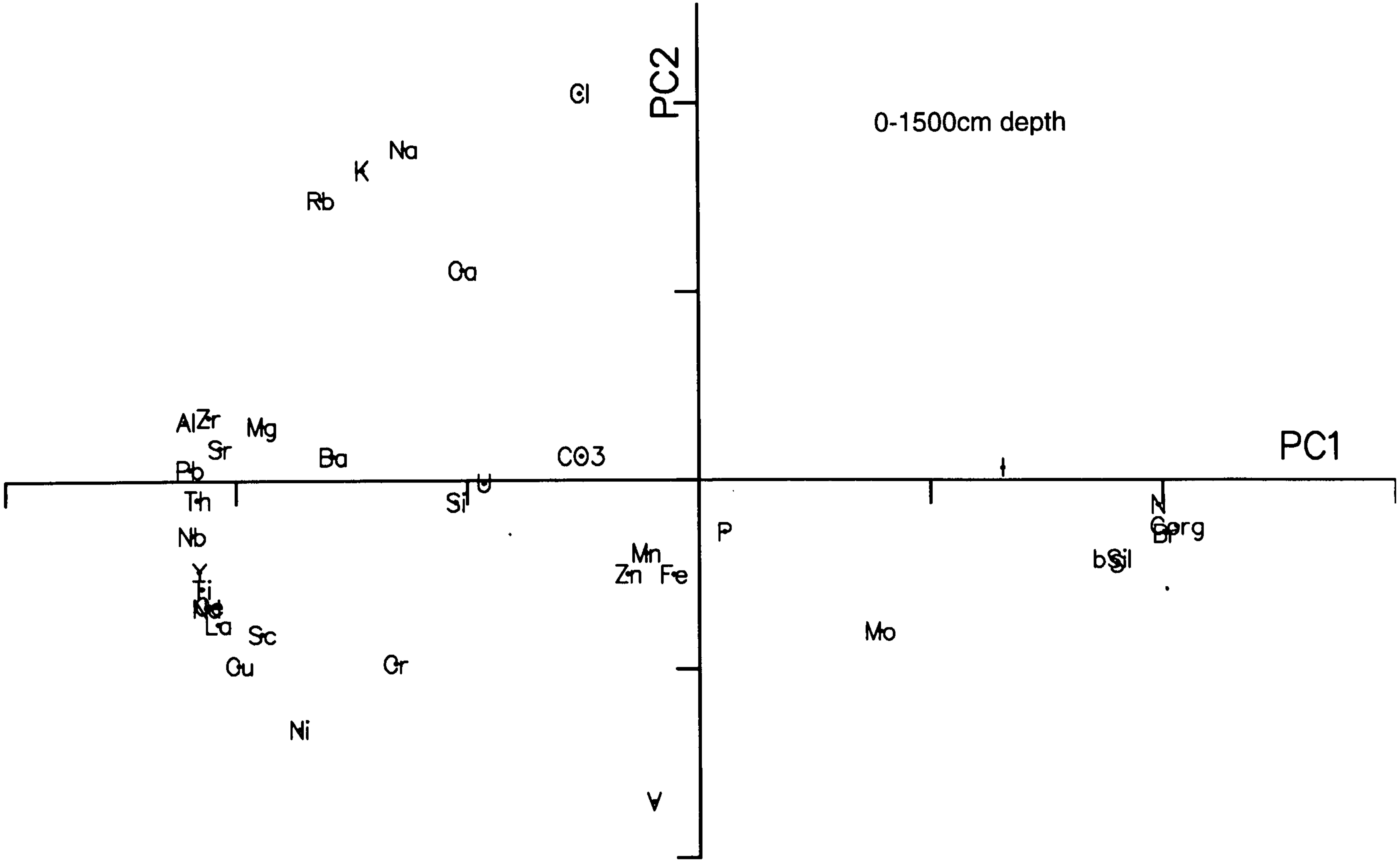


Fig. 3.3. PCA projection of elements measured on the upper 1500cm of core onto 1st and 2nd principal components axes

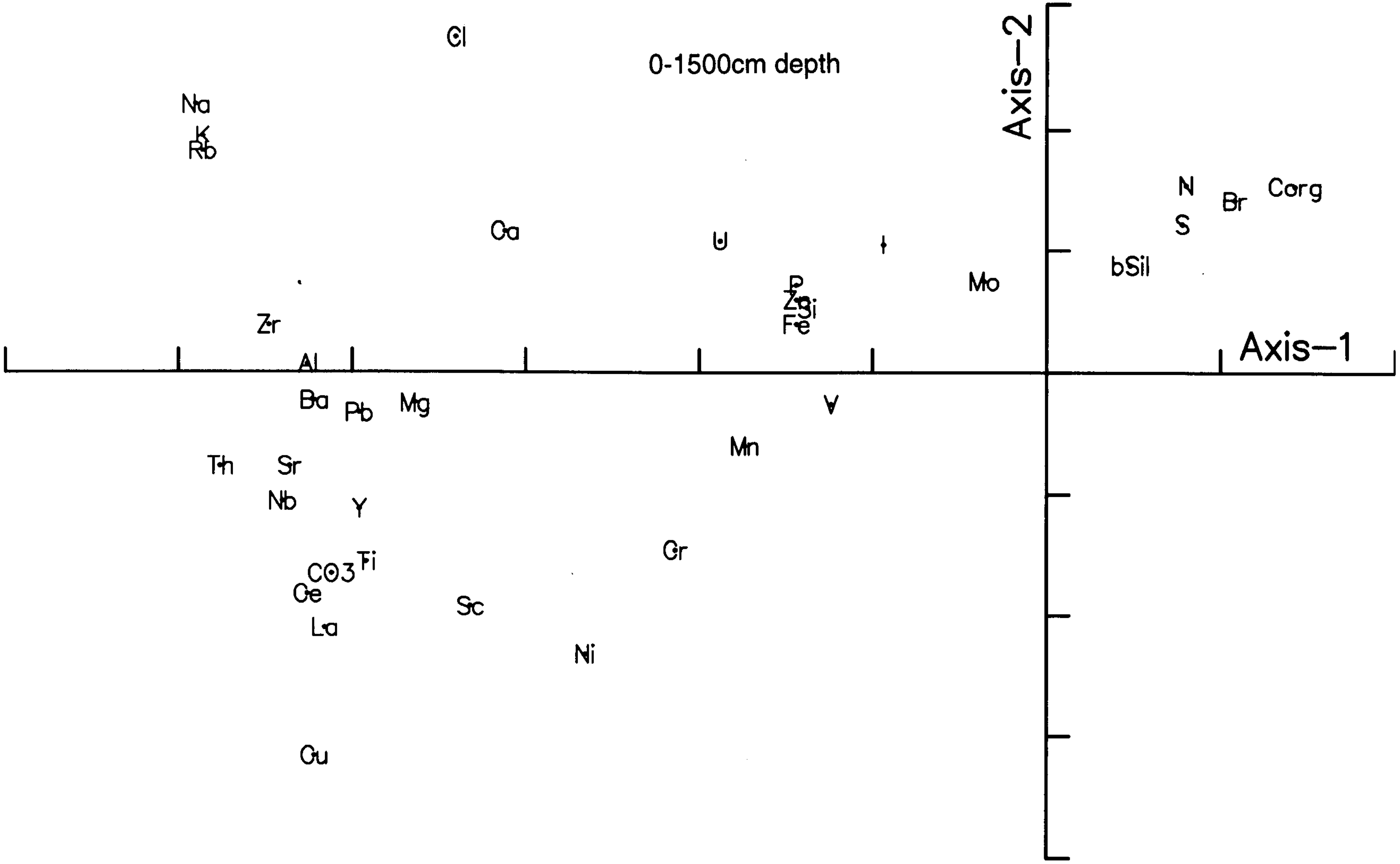


Fig. 3.4. Detrended correspondence analysis (DCA) projection of elements measured on the upper 1500cm of core onto 1st and 2nd principal axes of variance

e) -a broad group of elements (U, Zn, Mn, P, Fe, V, Mo) are largely derived from minerals locally, but show some association with organic matter and may reflect the influence of diagenesis upon the sediment. In particular, P, Fe, Mn and Zn form a compact subgroup probably reflecting vivianite content.

f) -inorganic carbon (CO3) reflects the presence of calcite and/or siderite and is situated in a field between Fe and Ca.

PC1 accounts for 52.7% of the variance exhibited by the dataset and appears to show a gradient between biological vs. mineral clastic inputs to the sediment. Thus, the largest differences in sediment geochemistry depend upon the relative contributions from these two sources. PC2 accounts for 12.4% of total variance and appears to divide elements strongly influenced by diagenesis from more conservative or immobile elements. The subsequent axes (PC3 to PC35) account for progressively less of the variance shown by the data set and do not display additional meaningful information. They will not be discussed further.

The same data from the upper 15 metres of the core was also examined by correspondence analysis using the DECORANA programme described by Hill (1979). Ordination was carried out on raw unweighted data using the default rescaling options. These results may be represented in a similar form to the PCA results above by a scatter plot of Axis-2 against Axis-1. Fig. 3.4. shows the results of detrended correspondence analysis (DCA) on the data. It can be seen that the two main axes of variance divide the chemical elements into similar groupings as before. There do exist some subtle differences between the PCA and DCA plots, but only the main broad groupings will be dealt with for this study.

Later, when geochemical analysis on samples from the remainder of the profile had been completed, the whole data set could be examined. Due to differences observed during preliminary examination of the lower part of the profile as compared with the younger part (comprising the uppermost 10-15 metres) it was decided to carry out a multivariate appraisal of the two sections separately as well as on the combined data. If the lower part of the profile (from 15 to 51 metres) is now looked at with the PCA method, a similar grouping of elemental variables is seen (Fig. 3.5.), albeit with certain differences.

a) -Corg, Br and biogenic silica remain in a grouping representing biogenic contributions, but S and N have moved towards the lithogenic pole.

b) -the band of elements previously extending from Ni to Zr appears as a more compact group and has re-ordered to some extent.

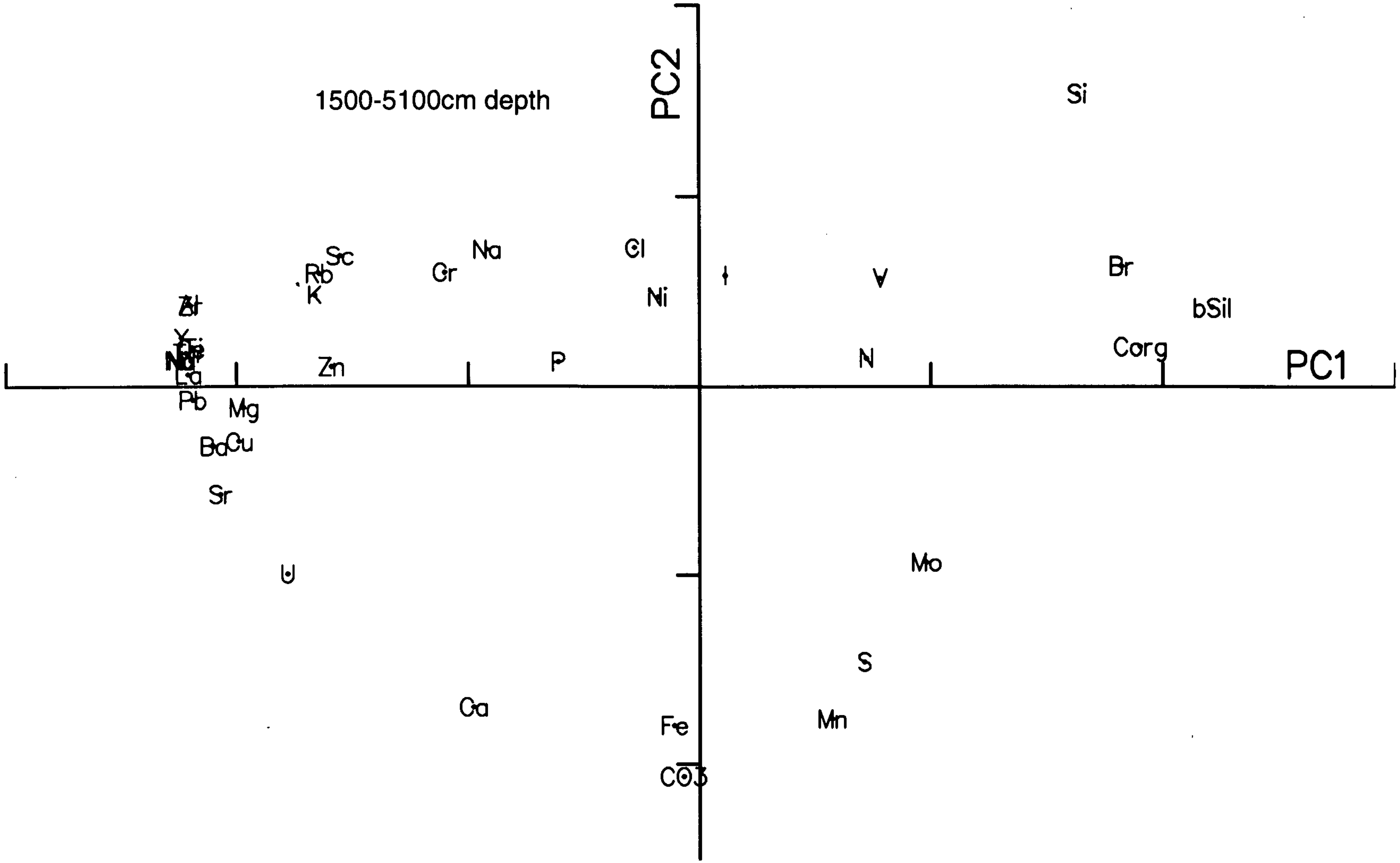


Fig. 3.5. PCA projection of elements measured on the lower 3600cm of core onto 1st and 2nd principal components axes

c) -the association between Cl and the alkali metals appears to have broken down and these elements are now somewhat dispersed.

d) -the broad group of elements possibly associated with diagenetic processes now includes mainly Mo, S, Mn, CO3, Fe, V and N. These components could reflect the contribution from phases such as iron sulphides, siderite and calcite. It is suggested in Chap 4a and Chap 4c that N may experience diagenetic enrichment too. P appears to behave more conservatively, lying closer to the lithogenic pole.

Again, Axis 1 shows heavy weighting between indicators of biological vs. minerogenic input and accounts for 50.6% of the total data set variance. Likewise, Axis 2 (12.4% of the total variance) seems to separate conservative from mobile elements.

Examination of the data in Q-mode allows the samples to be classified into different facies. It is possible to crowd all the samples (with their depth labels) onto a similar form of scatter plot and to draw facies boundaries around groups of points. Alternatively, the data may be viewed by plotting sample loadings for just one axis against sample depth. This requires the two main axes of variance to be looked at separately, but shows the sample properties in relation to their core stratigraphy more clearly. Fig. 3.6. shows the sample loadings from PC1 (reflecting biological vs. clastic phases of deposition) plotted against sample depth. In this plot the PCA loadings used are taken from PCA analysis of the whole core data set. As a working hypothesis it is suggested that periods of climatic amelioration are reflected by more biologically dominated sediment geochemistry and high positive scores on Fig. 3.6. Periods of downturn are indicated by more clastic dominated geochemistry and show low scores on Fig. 3.6. This signal is made spiky by the presence of tephra layers (see Chap 2/Chap 4b). As would be expected, the Holocene period covering the upper 800cm has consistently high sample scores on this profile. The trends on this 'composite' geochemical profile are later used in the discussion regarding the age of the core sequence. It will also be suggested that the PC1 sample score against depth profile strongly resembles palynological indicators for climate change obtained by W. Watts and J. Allen (see later in this chapter).

Fig. 3.7. shows sample scores from the subsequent PC2 axis plotted against sample depth. This component appeared to separate diagenetically mobile elements from immobile conservative elements in R-mode. When the sample stratigraphy is viewed it is found that high scores are associated with tephra-rich samples. These contain high concentrations of immobile alkali metals which have been given strong positive weightings on PC2.

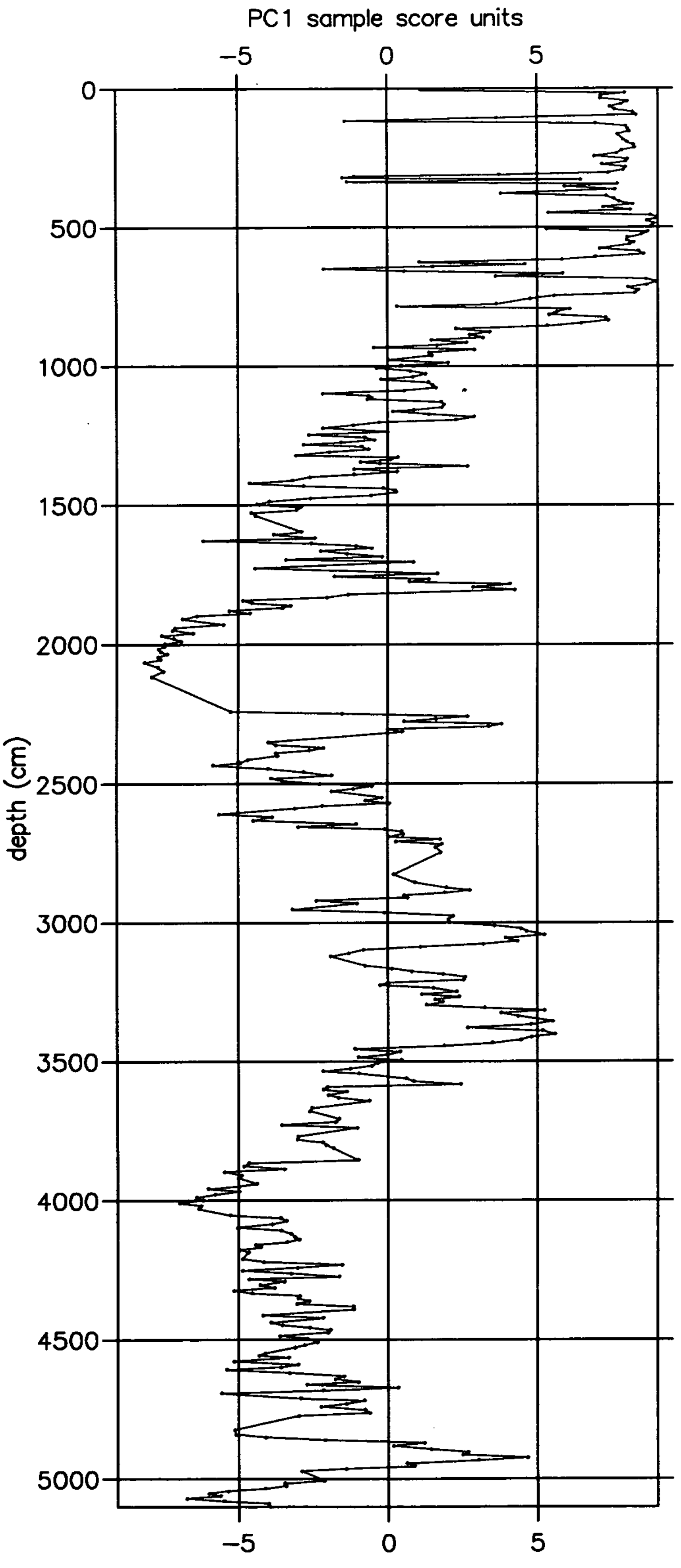


Fig. 3.6. PCA analysis of bulk geochemical data showing sample scores for the 1st principal component (PC1) against sample depth

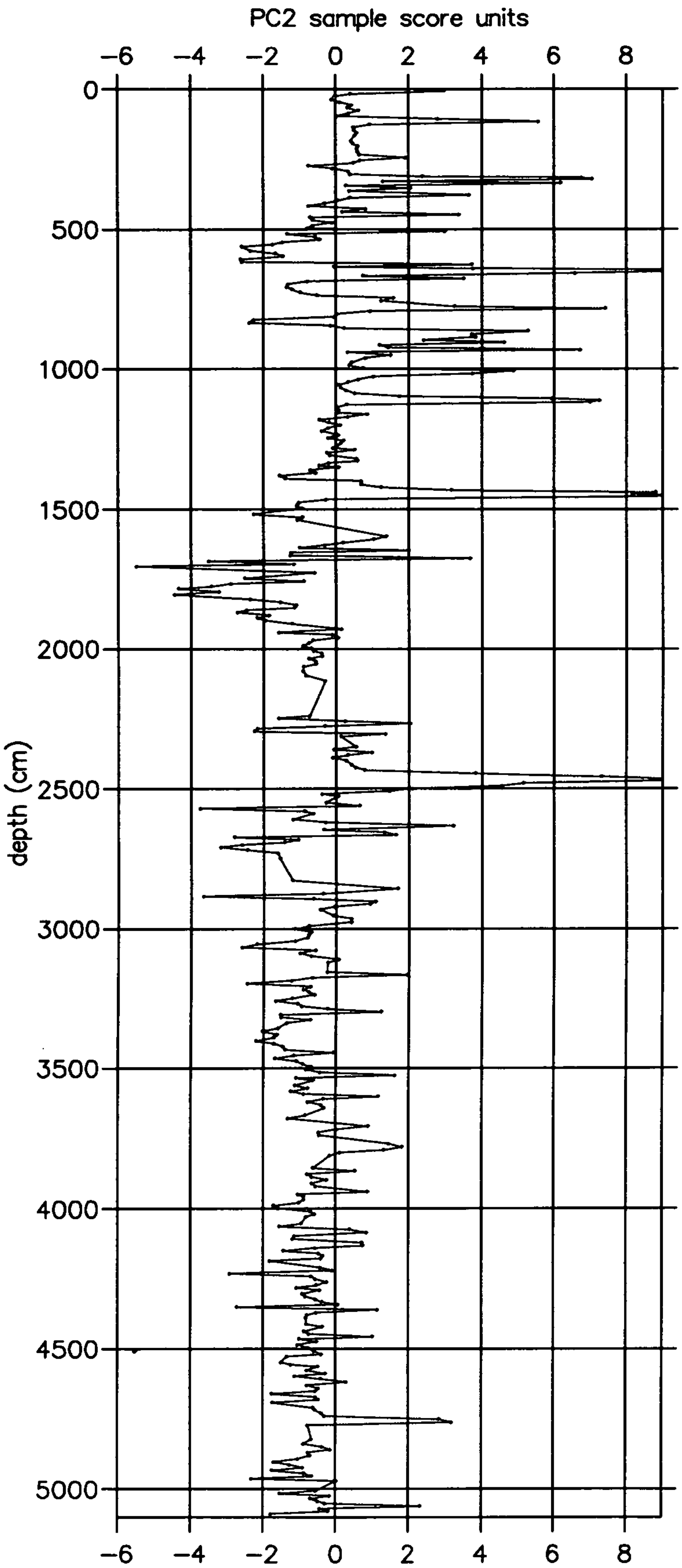


Fig. 3.7. PCA analysis of bulk geochemical data showing sample scores for the 2nd principal component (PC2) against sample depth

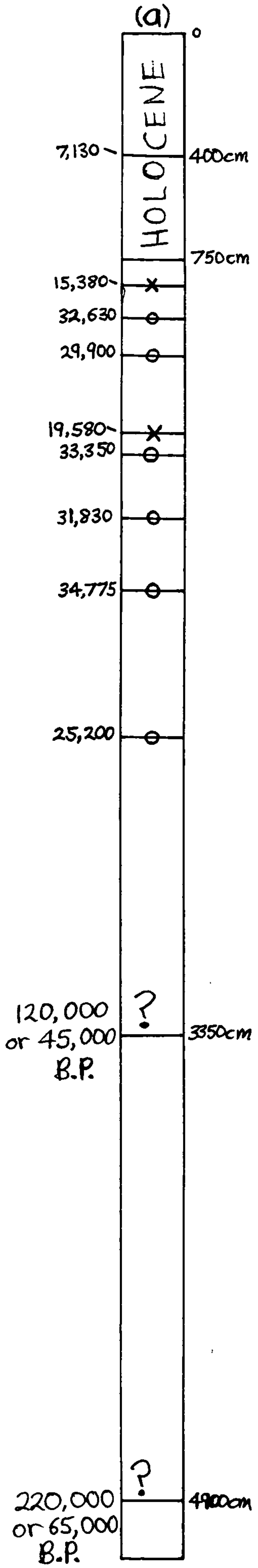
This information provided by a preliminary multivariate appraisal of the data appears to be useful in objectively identifying a small number of element associations which can be related to different aspects of the sediment contributors. This will help to order the forthcoming discussion of the geochemistry in Chaps. 4a-c. It has also provided a working summary of the core stratigraphy (PC1 sample scores against depth). Multivariate analysis might be used to search for further hidden meaning in the data set and to remove extraneous variation where specific information is sought (e.g. Marcotte and Fox, 1990), but the geochemical discussion will now be returned to in terms of individual components in the next chapter.

DATING OF THE SEQUENCE

Uncorrected radiocarbon dates made on the 1990 core sequence are presented in Fig. 3.8a. The second part of the diagram (Fig. 3.8b.) shows new dates made on two samples taken from earlier marginal cores. Information concerning the error bars associated with these dates and the initial sample preparation for the a.m.s. dated samples is given in Appendix 1. Tephra samples for Ar-Ar dating have also been submitted by Judy Allen at Durham University, but results from this are not yet avaiable. Fig. 3.9. shows an earlier suite of radiocarbon dates from the published work of Watts (1985) and includes some accompanying palynological data.

As can be seen, there are major discrepancies amongst the ages shown. Firstly, the sequence of six a.m.s. dated samples from 945cm, 1074cm, 1403cm, 1618cm, 1853cm and 2351cm depth all show a similar age of around 30,000 years B.P. Secondly, in both Watts (1985) and in the 1990 core, bulk radiocarbon dates appear excessively old. In the former case the Holocene boundary, denoted by an abrupt rise in birch followed by oak pollen (Fig. 3.9.), is bracketed by bulk dates of 18,290 and 21,200 years B.P., while in the present core the Holocene boundary at 750 or 850cm depth dates at around 15,000 years B.P. Moreover, in the 1984a and 1988 cores the samples dated were presumed to lie in the glacial-Holocene transition between 14,000 and 10,000 years B.P. (W. Watts, pers. comm.), but give ages of 23,670 and 30,460 years. Such data conflicts with other studies from southern Europe (Behre, 1989; Huntley and Birks, 1983) which date the onset of the Holocene interglacial close to the normal 10,000 years B.P. age, and suggests the presence of 'dead carbon' in the sediment.

Olsson (1986) reviews the potential causes for contamination by both young and old, inert carbon. The sediments of a lake represent a complex mixture of carbon from internal and



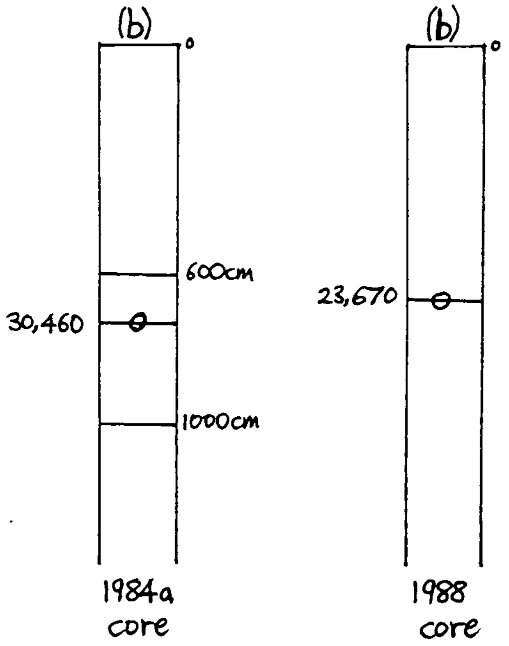


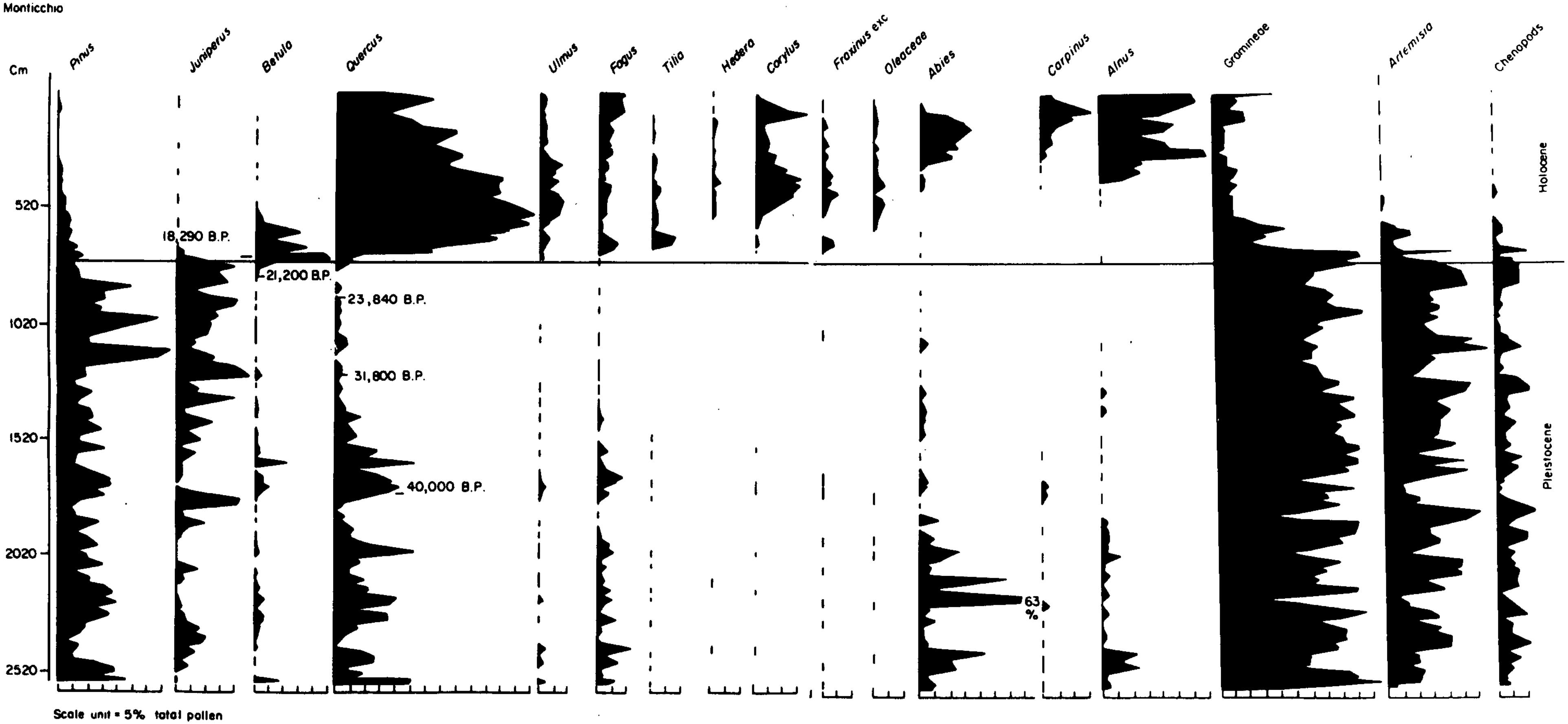
Fig. 3.8. Dates on the new core sequence (a), and on earlier marginal cores (b). The Holocene boundary in the earlier marginal records is thought to occur around 600-700cm depth (W. Watts, pers. comm.)

key: —o— macrofossil a.m.s. date

—×— conventional date on bulk sediment

(errors on dates given in Appendix 1)

Fig. 3.9. Previous dating and palynological work on Monticchio (modified from Watts, 1985)



external sources, but the two main possibilities for inclusion of dead carbon are thought to be:

1) reservoir/'hard-water' effects
2) inwash of older carbonaceous material

Attempts to overcome these effects have included the use of a.m.s. dating on selected macrofossil fragments. In the light of Watts' excessively-old bulk dates from his 1985 paper, it was decided to try this selective approach on the new core. It is of course necessary to ensure that the macrofossils submitted have not been susceptible to the 'hard water effect'. This is best done by selecting material of known terrestrial affinity, such as birch fruits or pine needles. Although birch fruits exist in the Monticchio core material they may not occur in sufficient quantity to provide the >1mg of carbon needed to furnish a reliable date. This is a greater problem for the 1990 cores since they were taken from much further offshore and would receive less input of birch fruits etc. from catchment vegetation than the sediments accumulating at the lake margins. As an alternative, bryophyte fragments were selected from layers which are rich in this type of macrofossil. Examination of the fragments by Brian Huntley and Judy Allen at Durham showed the presence of both shallow fen type and probable deep water genera. From the assemblages present, the former types were picked out for dating, including the genera Calliergon and Scorpidium. Broadly speaking, these varieties of moss are believed to take their carbon from **atmospheric CO_2** as opposed to deeper water genera (such as Fontinales) which could assimilate carbon from the lake bicarbonate/dissolved CO_2 reservoir or from CO_2 sources due to organic matter decay in the sediments. Unfortunately the dates produced are anomalous and do not even show stratigraphic concordance.

The hard-water effect is believed to affect many lake systems. The classic case is of a lake situated in a catchment of limestone or carbonate geology. Dissolution transfers some of this ancient carbon into the lake waters as bicarbonate. This adds to lake bicarbonate formed through normal exchanges with atmospheric carbon dioxide. The input of ancient carbon gives the lake water bicarbonate reservoir a lower ^{14}C activity than that in equilibrium with atmospheric CO_2 concentrations and this depletion is maintained due to insufficient lake circulation. Therefore plants assimilating from this source will date too old. The effect has also been observed in deglaciated terrains which do not necessarily lie in limestone areas. Due to the presence of carbonate material in glacial till, the early sediments of some postglacial lakes give anomalously old dates, but these anomalies may decrease as soil and vegetation development change the catchment (e.g. Bradley, 1985 and refs. therein). The hard-water effect is difficult to quantify and, as the last point illustrates, the associated error may change over time. According to Shotton (1972) "it is usually stated that the maximum possible error is equivalent to the half-life of ^{14}C, 5570 yr, but rarely amounts to as much as this..." Most authors simply recognise that the factor varies amongst lakes depending on hydrologic and chemical conditons (e.g. Stiller, 1988).

Recently, results from ^{14}C measurements made on living plants in Lago Grande and Lago Piccolo suggest the presence of a significant hard water effect (J. Allen, pers. comm.). This is evidenced by samples of aquatic vegetation (Ceratophyllum and Myriophyllum) which are thought to photosynthesise from the lake water reservoir showing dates of 2000 and 7300 years before present. In contrast, vegetation known to photosynthesise from atmospheric CO_2 (Nymphaea and Phragmites) showed essentially modern ages. As mentioned in Chap. 2, Lago Grande di Monticchio is situated in a catchment area of alkali basic volcanic rocks. These lavas and pyroclastics are essentially non-carbonate bearing, however investigation by Fiore et. al. (1992) indicates that the sequence is invaded by veins of calcite. More importantly, the emanation of juvenile CO_2 has been inferred from recent field observations at Laghi di Monticchio (B. Huntley, pers. comm.). This would have the potential for adding ^{14}C-free carbon to the lake water reservoir and maybe even influencing the local atmospheric composition. The possible volcanogenic CO_2 input effect on Monticchio may be difficult to quantify, but there is a strong suspicion that it is responsible for some of the errors observed. It is also to be noted that, several km from the lake, mineral water is extracted for local consumption and that this mineral water is slightly sparkling (-contains CO_2 from some source) as well as being rather salty. In addition to these recent observations, it should be remembered that carbonate precipitation occurred at Lago Grande di Monticchio during earlier periods, as evidenced by the presence of calcite and siderite in glacial parts of the sediment record.

In order to produce the probably large age errors encountered it would seem unlikely that the hard-water effect alone is responsible. In particular, the macrofossil samples appear strongly in error and are assumed to have been outside the influences of the hard-water effect. It would appear that the inwash of older plant material is another likely process for explaining the suspected artificially high ages.

It may be the case that the dated bryophyte fragments have been reworked from an older (30,000 year interstadial?) growth. Perhaps change in lake water level or a more catastrophic erosional event such as storm runoff led to their redeposition. The mosses appear in well-defined layers up to several cm thick in the core sequence and were initially thought to have developed as in situ mats on a shallow lake bed or to have grown near to the shoreline and become redeposited soon afterwards. It appears unusual that the bryophyte remains should be reworked into a fairly uniform layer thousands of years after they grew. The reworking process could be aided by the instability of the lake environment which has experienced volcanic activity and earthquakes with potential for disturbing material that has resided in the catchment zone for a long period of time. From the palynological record (see next section) it is clear that the crater has experienced considerable changes in the quantity and quality of vegetational cover (perhaps affecting soil stability) and probably changes in climatic conditions such as precipitation and storminess. These factors could also offer mechanisms of redeposition.

If the reworking hypothesis is correct for the selected bryophyte fragments, then it could also assist in explaining the older ages seen in the bulk dates. Bulk sediment could easily contain some remains of older organic carbon or graphite. This contamination could include anything from infinitely old (highly residual kerogen/graphite) to plant debris merely a few thousands years older than the contemporaneous sediments. Observation of organic residues prepared for palynofacies examination (see Appendix 1 and Chap. 5) shows the presence of dark, resistant lignaceous material in many sections. This is one possible contributor of old carbon to the bulk sediment. It is interesting to note that the bulk dates taken on the new 1990 core show probable age errors considerably lower than the probable errors on the Watts (1985) marginal core. A possible explanation for this is the fact that the sediments in the earlier marginal core have been contaminated with a higher proportion of reworked material due to their closer proximity to the crater source zone of such material.

Olsson (1986) shows that contamination by material younger than the sediment being dated gives a considerably larger error than the effect of contamination on young material by old carbon. Therefore to cause an appreciable error in the older direction requires a relatively large degree of contamination. For example, contamination to a degree of 50% with very old material is required to cause a sample to date 5570 years (i.e. one half-life) older than its true age.) Very old or infinitely old carbon may be taken to imply material older than 50,000 or 100,000 years in this case. This level of ^{14}C activity is beyond the detection range by present analytical techniques and thus is effectively of infinite age. Table 3.2. shows the amount of contamination by such infinitely old material required to produce dates between 400 and 11,000 years older than the true age of a sample.

The bulk dates from the 1990 core material may be up to 5000 years too old implying that 40-50% of dead carbon could be present. And an even greater proportion of contamination

contamination	age error (years)
5%	400
10%	850
20%	1800
30%	2650
40%	4100
50%	5570
75%	11140

Table 3.2. Age errors associated with varying amounts of inert carbon (modified from Lowe and Walker, 1984)

could be present in the Watts (1985) profile. In this case the dates surrounding the Holocene boundary may be up to 10,000 years out. It seems probable that part of the total error is caused by a contribution from hard-water phenomena affecting the contemporaneous plant matter, but it is also likely that a significant amount of secondary material is present in the Monticchio sediments.

At the time of writing no further radiocarbon dating of the sequence is planned, although the Ar-Ar dates are eagerly awaited. There appears to be a real dating problem at Monticchio, probably due to reworking, and the use of selected macrofossils may not be the best approach in this environment. Indeed the evidence so far shows that the macrofossils selected give worse age indications than the bulk sediment, which is relatively unusual. Carbon dating may best proceed by using bulk sediment samples, preferably with sieving treatment to remove coarser organic particles, such as woody fragments, which may be unreliable constituents to include. The additional step of separating humic (NaOH soluble) and insoluble humin fractions and perhaps dating both is worth pursuing. This has been shown to be particularly effective in identifying valid radiocarbon ages by Olsson (1991) and refs. therein. The dates made on the humic fraction are generally more reliable for lake sediment material such as gyttja (Olsson, 1991). Lowe et. al. (1988) go further and recommend a.m.s. dating of five organic preparations (conventionally pretreated sub-sample, humic acid fraction, total unbound lipids, macrofossil cellulose and bulk cellulose residue) together with normal scintillation counting of a bulk sample from the same zone. However, this requires much greater resources and might not get round problems such as redeposition. In this kind of study, Creer (1991) emphasises the importance of using sequences of samples rather than a small number of isolated dates.

AN AGE MODEL FOR THE SEQUENCE

At present there exist two possible age models for interpretation of the sequence:

1) the core covers up to the last 70,000 years with the zone from 2700 to 3400cm representing a 30-45,000 year interstadial and the 4900cm zone representing a minor interstadial some time after the major St. Germain II interstadial. In this case there are no earlier interglacial periods recorded and the record of the last glacial period is highly detailed: -the "young alternative"
OR
2) the core covers the past 200-250,000 years and thus includes the Eemian interglacial at 3400cm and a preceding interglacial which is perhaps equivalent to oxygen isotope Stage 7 at 4900cm depth: -the "old alternative"

To these two alternatives might be added the possibility of varying time gaps in the record caused by erosive removal or non-deposition. So far, no positive evidence for periods of desiccation or emergence has been found (Chap. 2). It is also believed that sediment focusing (Lehman, 1975) is not an important process in Lago Grande (B. Zolitschka, pers. comm.). The lake lies within a small, sheltered catchment where wave action, a principal agent of sediment redeposition, is probably minimal. If large quantities of the sediment pile had been redeposited in deeper parts of the lake, then the 30 metre deep cauldron feature (Fig. 2.3.) would most likely have been filled in with material from the rest of the lake which covers a large shallow shelf area. It should nevertheless be remembered that this deep pit may represent a relatively young feature in the overall lake sedimentation history and could be *partially* filled with resuspended sediment. The turbiditic and slump features that appear in the record show that physical disturbance has taken place at certain times. It is possible that initial erosive processes connected with these events (particularly the two large slump units) may have removed a few hundred or thousand years worth of sediment record at the slump base.

With the radiocarbon dates that are available, we cannot conclusively eliminate either of the age possibilities. For one thing, these dates appear to contain errors and cannot be applied confidently. And, even if correct, it is not possible for radiocarbon dating to reach the critical lower part of the core (which is generally accepted as extending some way beyond 40,000 years B.P.).

It is hoped that the varve-analysis work being carried out by Bernd Zolitschka in Trier may clarify the dating problem. Although thin section preparations show that laminae suffer from periods of obliteration or non-formation over major sections of the profile, *enough* of the record may contain laminae of one form or another to permit a reasonable age estimate. Unfortunately, systematic counting of these micro-layers has only just begun and the work involved will take at least two more years to complete.

These relatively objective methods of dating have been accompanied by more subjective correlative approaches from other groups working on the 1990 core sequence. Due to the presence of numerous (and sometimes very thick) tephra layers in the record it was hoped that analysis of the volcanic glass fragments would allow these layers to be fingerprinted against well documented eruptions. Initial work has been done on several of the thicker layers from the upper 15m of the profile (Newton and Dugmore, 1993). These have been linked with a source in the Campi Flegrei province around Naples, but it has not been possible to identify with certainty which particular eruption they came from. A major problem in this field is the lack of published data on Italian eruptions to make correlations with. On the other hand, if the sedimentary record from Monticchio was well-dated by other means, the tephra layers here might provide an excellent sequence for future sites to be correlated against. It is interesting to note that the upper part of the core records a high number of visible tephra layers compared with the sediments below 25 metres depth (see Figs. 2.4. and 6.7.), and perhaps indicates a shift in the amount of regional volcanicity. At present, the Monticchio tephrochronological studies have shifted to the group working at Rome, but no results are known so far.

Attempts to date the core from the sediment pollen record have been made by Watts (1992) and by Huntley and Allen at Durham (unpubl. work). The results of their palynological work are illustrated in Fig. 3.10. and discussed further towards the end of this chapter.

Other attempts at dating have been made by correlating palaeomagnetic measurements with type palaeosecular variation records from Europe and with the marine oxygen isotope curve (Turton, 1993). The magnetic intensity records from Monticchio appear to be quite weak, probably because the sediments are dominated for large areas by organic matter and biogenic silica. These components strongly dilute the terrigenous clastic fraction which carries the magnetic signal. As a consequence of this, the curves for parameters such as palaeointensity are not strongly defined and can be correlated in more than one way with other records. Environmental magnetic parameters, such as magnetic susceptibility, show the predicted inverse correlation with organic carbon content and with biogenic silica content. Like organic carbon they can be correlated with climatic records from other sites, but they do not reveal the breadth of information that is available from a series of geochemical analyses. The correlation of organic carbon with other lacustrine records will be dealt with in Chap. 4a.

Before discussing the bulk geochemistry in Chaps. 4a-c, some of the arguments are presented for the rival age hypotheses:

<u>The young alternative</u>

The young alternative arose following initial examination of the sedimentology and micro-sedimentology (Zolitschka and Negendank, 1991) and applying ideas gained from the study of Eifel maar lake deposits. From pilot investigations of the upper 900cm of the sequence, laminae of annual nature were confirmed. In this part of the core the laminae varied from 0.25 to 1.25mm in thickness. Using an average sedimentation value of 0.75mm/year the Holocene would begin at 750cm depth, which is in agreement with the abrupt rises in arboreal pollen and organic carbon content observed. If this sedimentation value is extrapolated to the whole 51 metres of core then the base dates at 68,000 years B.P. This exercise obviously ignores the effects of compaction (which might condense the lower parts of the sequence), but it was thought that this would be offset by Pleistocene sedimentation rates being higher than those in the Holocene. It was also suggested that several metres of the record (including slump units, tephra layers and turbidites) would probably have been deposited rapidly and not represent substantial time intervals. With this model, the zone of clastic-rich sediments between 1900 and 2250cm was initially correlated with the last glacial maximum (18-20,000 years B.P.) and interpreted as a time of increased soil erosion and/or aeolian activity in response to a barren steppe-like vegetation. This was later re-interpreted as a period of high rainfall under conditions of low vegetational cover, somewhere between 20 and 30,000 years B.P. (Zolitschka and Negendank, in prep.). The climatic amelioration suggested by the more biogenic sediments between 2700 and 3400cm depth would correlate with a 30-45,000 year interstadial event or oxygen isotope stage 3. The signature of this climatic amelioration is nowhere as strong as the Holocene (which should represent type interglacial conditions) and thus the zone must merely represent an interstadial event. The climatic amelioration suggested by the sediments around 4900cm depth would correlate with an earlier interstadial event, although not the pronounced St Germain II/oxygen isotope stage 5a period. Therefore the climatic amelioration at 4900cm is regarded as an interstadial of around 60,000 years age/within oxygen isotope stage 4. This implies that the St Germain II (and for that matter the Eemian interglacial) may be present some distance below the base of the 1990 core, perhaps beyond 60 metres depth.

The old alternative

Suggestion that the core might encompass the Eemian and a preceeding interglacial was made by Watts (1992) from palynological evidence. This interpretation has since been retracted somewhat (W. Watts, pers. comm.) in favour of the young alternative. From the geochemical and sedimentological evidence, however, this older model is favoured by the present author and it will be fully incorporated in the subsequent discussion of the sediment geochemistry.

Arguments in favour of the older alternative are introduced by presenting evidence against the previous model. Firstly, the young model assumes a mean sedimentation rate of around 0.75mm/year for the glacial period, i.e. comparable to the mean Holocene rate of 0.75mm/year. It has been suggested that an increased glacial sedimentation rate may result from a reduction in vegetation cover permitting increased erosion of catchment soils and/or transport of aeolian dust. However, it is to be noted from analysis of the Holocene zone (Chap. 4a) that these sediments are dominated by organic matter and biogenic (diatomaceous) silica components and that an extremely low amount of clastic material (<10wt%) is present. The Holocene sediments are also particularly uncompacted since they contain over 80wt% water (Fig. 2.5.). From this information, it would appear that the sediment accumulation rate value of 0.75mm/year does not give a reliable measure of the accumulation of *eroded clastic material* for the overall record. A much lower figure should probably be evaluated for lower parts of the core because the basic Holocene accumulation rate is made artificially high by conditions of high autochthonous productivity. It is still to be expected that the underlying glacial deposits would have experienced a higher accumulation rate of the terrigenous clastic fraction, but this should be compensated for (or perhaps strongly offset) by the greatly reduced addition of organic matter and biogenic silica resulting from lower internal productivity during the glacial period. Increased compaction due to overlying material would also condense the lower sediment zones relative to the Holocene. This is evidenced by lower water contents (around 60wt%) for this part of the core (Fig. 2.5.). The idea that the Holocene accumulation rate is considerably higher than that of the preceding glacial period is in agreement with conclusions from a survey of sediment accumulation rates in North American small lakes (Webb and Webb, 1988), where rates of inorganic sediment accumulation were found on average to be lower than those of organic sediments. The survey also looked at late-Pleistocene vs. Holocene subsets of data from these mid-latitude lake sites and found that the average accumulation rates for the two

subsets were 0.52mm/year and 0.81mm/year respectively. The results were interpreted in terms of depressed temperatures during the glacial resulting in lower productivity in the basins, leading to lower sediment accumulation rates.
Possible support that the glacial sediments are condensed and cover a relatively long time interval comes from microscopic investigation of the sedimentary laminae. The laminae for the Holocene section have already been identified as being annual (Zolitschka and Negendank, 1991) and as having an average individual thickness of approximately 0.75mm. Pilot sections prepared from the Holocene zone were examined and compared with sections prepared from the late-glacial section. Within this latter zone, the laminae present differed from those of the Holocene and appeared to be several times thinner (perhaps around 0.2mm thick). This preliminary observation needs to be treated with caution as these older laminae have not yet been proved to be of annual nature and require careful counting work to be made on them.

The bulk radiocarbon dates made so far offer more equivocal support to the case for an older interpretation. A reasonable guess might be that in Watts (1985) the dates are on average 10,000 years too old, and for the 1990 core an average of 3,000 years too old. If these corrections are made, it turns out that 20,000 years B.P. lies somewhere close to 1500cm depth rather than at 2000cm where the clastic-rich sediments occur. The 1985 dates point more in this direction than those on the more recent core, but this involves the assumption that the sediment accumulation at the former marginal site is similar to that of the present core. There appear to be problems correlating marginal cores with the present shelf core (B. Huntley, pers. comm.), although profiles from both sites contain a similar thickness (around 700cm) of Holocene deposit. If an even bigger assumption is made that the Watts (1985) radiocarbon ages are *systematically* in error by a constant factor, it might be the case that the 30,000 years B.P. period is reached by 1800cm depth. This would hold the possibility for suitably low sedimentation rates to be prevalent in the glacial period. In opposition to these ideas, the presence of dates which are 'too young' to support the old age interpretation arises if the a.m.s. dated macrofossil samples are considered. In particular the 25,200 years B.P. date at 2351cm (Fig. 3.8.) conflicts with this model unless the sample in question has been contaminated with young carbon.

The sediment geochemistry as summarised by multivariate analysis may also provide an argument as it is noted that the three peaks in amelioration of 2700, 3050 and 3400cm depth (Fig. 3.6.) have a similar form to stage 5 of the oxgen isotope curve (ignoring for the moment the fact that they are of considerably reduced magnitude as compared with the Holocene).

This correlation would tend to fit with the old age alternative. Further discussion of the geochemical data will now be postponed until the next chapter.

If the four previous arguments are correct, this implies that deeper parts of the core (especially from 2250cm to the base) contain a sediment sequence much more condensed than the Holocene and possibly covering a very long time interval. These lower sediments contain only 40-60wt% water (Fig. 2.5.) and much lower concentrations of (autochthonous) organic matter (Chap. 4a), making clastic deposition a more significant control on sediment thickness. In order to reach an age of 240,000 years B.P. at the base requires sediment accumulation rates averaging 0.1 to 0.2mm/year in the zone below 2200cm depth. In Webb and Webb (1988), 95% of lakes surveyed showed accumulation rates between 0.16 and 2.15mm/year. It was also suggested that extremely low rates (<0.1mm/year) were likely to be associated with depositional gaps. In this context, 0.1 to 0.15mm/year is a particularly low rate for a small lake. On the other hand, this survey did not include sediments beyond those of late-glacial age and these examples are likely to be less well compacted than very old material. Also, Monticchio is characterised by a low catchment to surface area ratio (as described in Chap. 2) and low accumulation rates would be predicted. This has been demonstrated from other maars, for example Lac du Bouchet is believed to show accumulation rates below 0.2mm/year over large parts of its sediment record (Truze and Kelts, 1993).

An early interpretation of the pollen record, summarised in Fig. 3.10., suggested the presence of the Eemian interglacial at 3400cm depth (Watts, 1992). Incidentally, this work has placed the Holocene boundary at 850cm as opposed to 750cm depth, although more detailed pollen analysis together with improved dating control will be needed to clarify the exact position. Certain features diagnostic of an interglacial were recognised in the record around 3400cm. These included high percentages of tree pollen, the appearance of broad leaved thermophilous taxa, indications of the re-appearance of a reed swamp at the lake margins, and vegetational successions known to be associated with glacial to interglacial transitions. The record between 2700 and 3400cm was seen to 'mirror' stage 5 of the oxygen isotope record in a similar way to the summary of sediment geochemistry dealt with in the preceding paragraphs. Indeed, there is a strong consistency between the pollen and geochemical records in pointing to these zones of climatic amelioration (c.f. Figs. 3.6. and 3.10.). Although the reason why both records (particularly the pollen record which indicates change in the terrestrial environment i.e. much more directly climate) should show significantly lower signals for this interglacial than for the Holocene is difficult to explain, the profiles do appear to fit well against stage 5. During this early interpretation the zone around

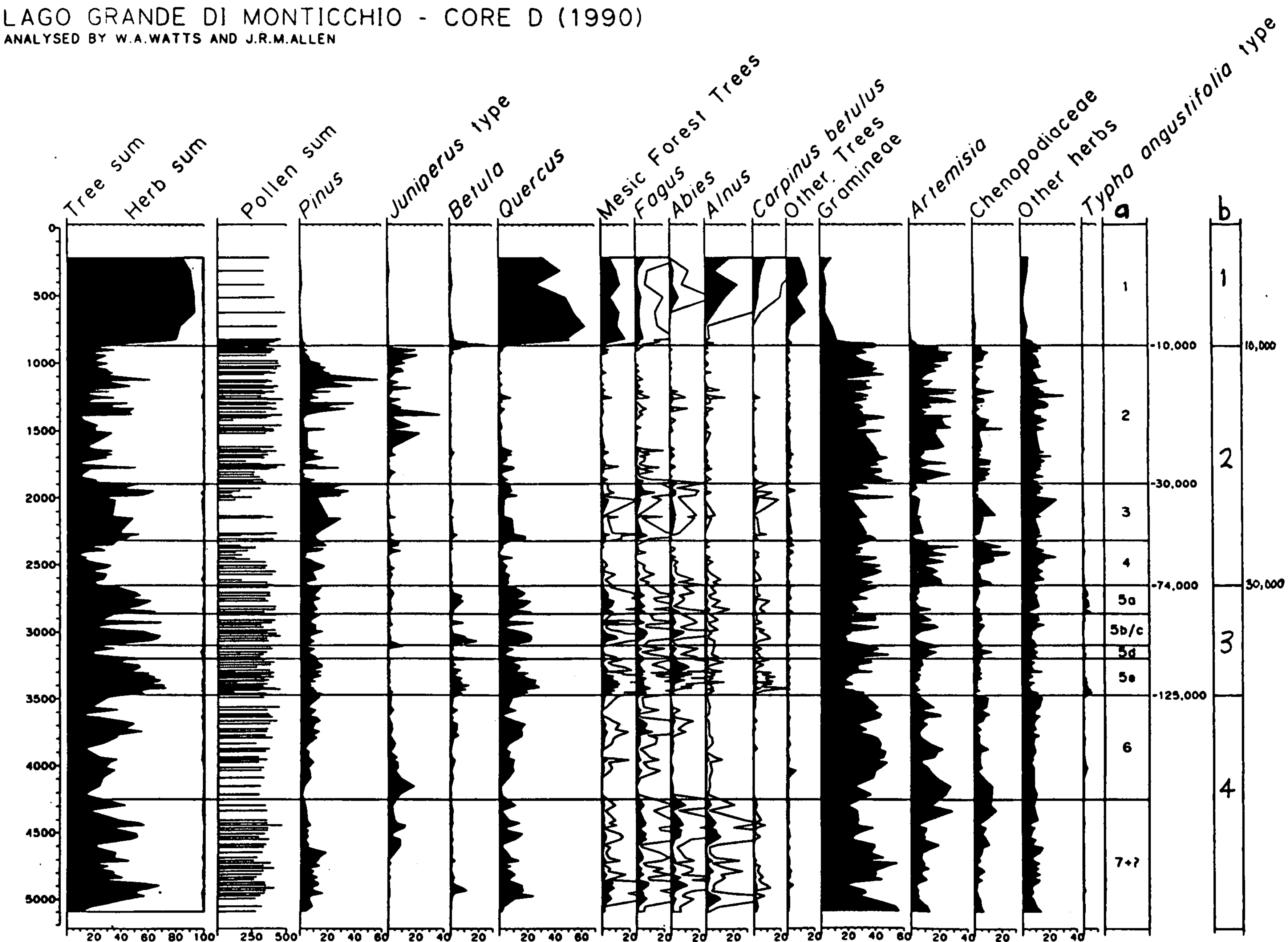


Fig. 3.10. Pollen diagram for 1990 core (Watts and Allen, unpubl. work) together with old (a) and young (b) age interpretations based on marine oxygen isotope stages

4900cm depth was placed in oxygen isotope stage 7 at around 240,000 years B.P. This zone also shows interglacial-like features, but was more tentatively interpreted as being such an event (Watts, 1992).

Subsequent reservations about the presence of the Eemian have altered the palynological interpretation in favour of the young age model. It is now suggested that the pollen record is a highly detailed one extending back through late and mid-glacial times (W. Watts, pers. comm.) In this alternative explanation, the fluctuations seen in the zone between 2700 and 3400cm are tentatively associated with Heinrich events (Bond et. al., 1992.) This relationship has previously been suggested from Florida lake sediment records (Grimm et. al., 1993; Watts et. al. 1992).

The two possible age models (a and b) are shown in terms of correlatable marine oxygen isotope stages beside the pollen diagram in Fig. 3.10. Again the need for objective dates must be emphasised.

With this unresolved picture in mind the sediment geochemistry will now be dealt with in more detail.

CHAPTER 4a

BIOGENIC COMPONENTS OF THE SEDIMENTS

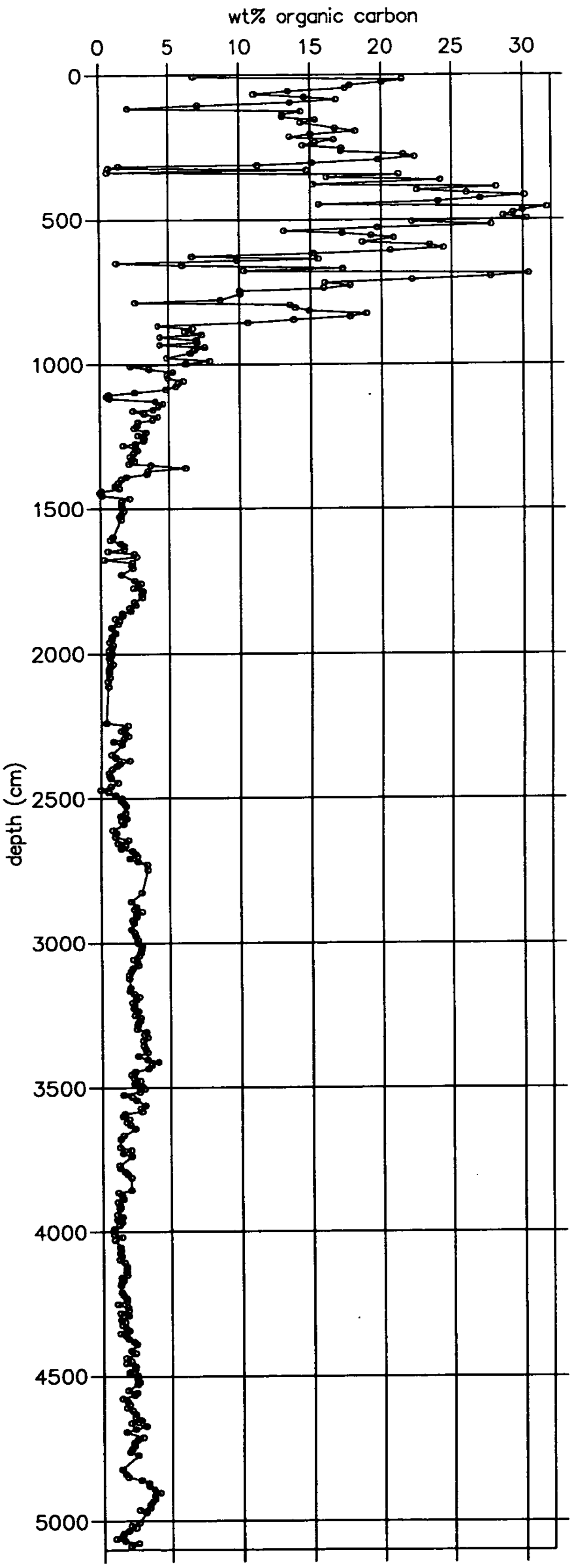
ORGANIC CARBON

Many lake sediment studies have considered organic carbon to be the most important geochemical variable. Mackereth (1965; 1966) was one of the first to measure a wide range of elements on sediments from the English Lake District. In a series of lakes he found that the carbon content rose rapidly after the cessation of glaciation to reach a maximum in the first half of the post-glacial period. This association between rise in organic carbon and climatic improvement has been found in many other large and small lakes, including European maar-lakes (Brown, 1991; Truze, 1990). However care must be taken in the widespread extrapolation of this relationship which was originally based on lakes with a predominantly oligotrophic character. The lack of a simple direct relationship with climate (e.g. temperature or rainfall) can be illustrated by the case of two lakes from as widely different areas as Arctic Canada (King, 1991) and equatorial Africa (Giresse et. al., 1990) both containing 10wt% organic carbon content in their sediments. Local factors are clearly significant influences on organic carbon content.

If the Monticchio profile is examined (Fig. 4.1.), organic carbon values appear relatively low (<4wt%) between the oldest sediments at 5100cm up to around 1500cm depth. Between 1500cm and 860cm depth, values increase gradually, towards 7wt% C. Above 860cm depth, there is a sharp rise to much higher organic carbon contents, and from here to the surface values remain consistently above 15wt% C. These basic differences are easily related to visual examination of ther core sections (Fig. 2.4. and Plates 3-5.). In particular, the abrupt rise above 860cm is seen as a change from pale brown muds to intense black gyttja and subsequent dark brown gyttja. An immediate feature in this youngest part of the sequence is the presence of a number of pronounced negative spikes. These are due to tephra layers covered in the sampling profile. The main tephra layers, from visual examination, have been marked on Fig. 4.2. for comparison. The pervasive presence of tephra layers adds noise to the probable underlying climatic signal.

It is now worth examining these three main areas of the profile separately and in more detail.

1) 0-860cm. The upper section begins sharply with a rise from 7wt% to 18wt% organic carbon over just 30cm. The first maximum occurs at 825cm, after which there is a decline in organic carbon over the next metre or so. A tephra layer (organic carbon poor material) is also situated within this zone of decline. Above 750cm the organic carbon profile risely sharply to even higher values than before. A maximum of 30wt% C is reached at 680cm. The following zone is strongly affected by "noise" from numerous tephra layers. The background



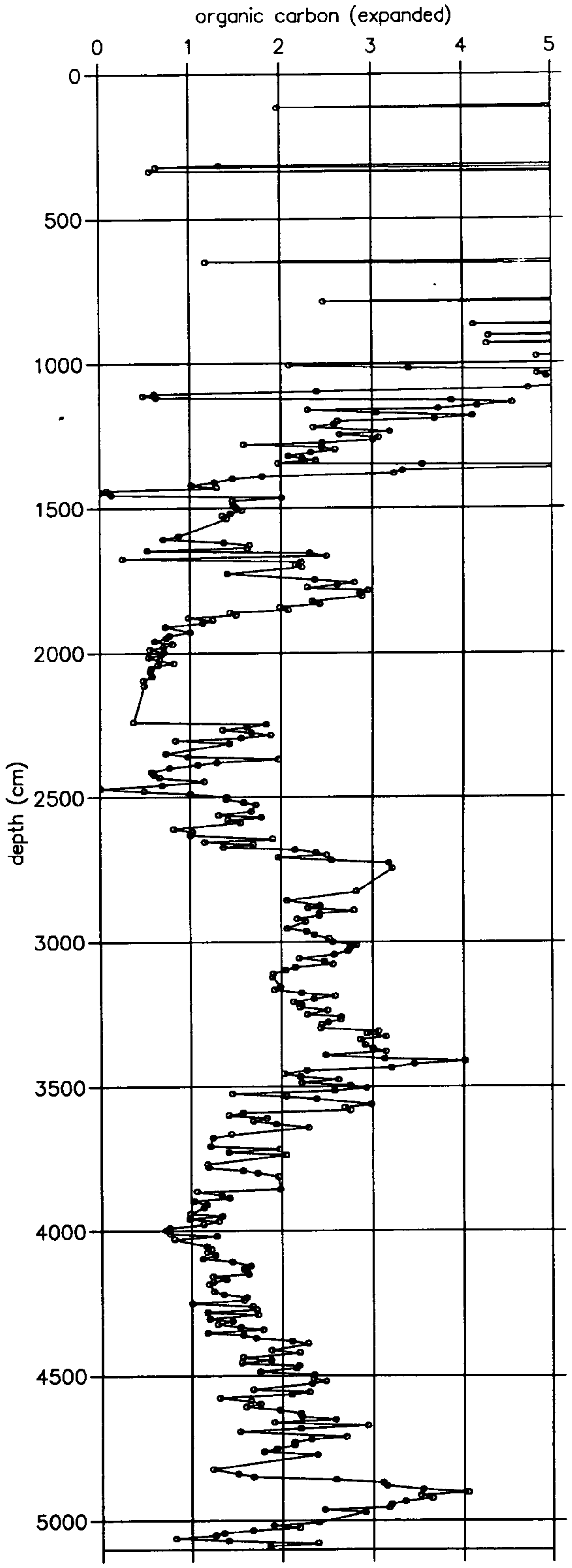


Fig. 4.1. Organic carbon content

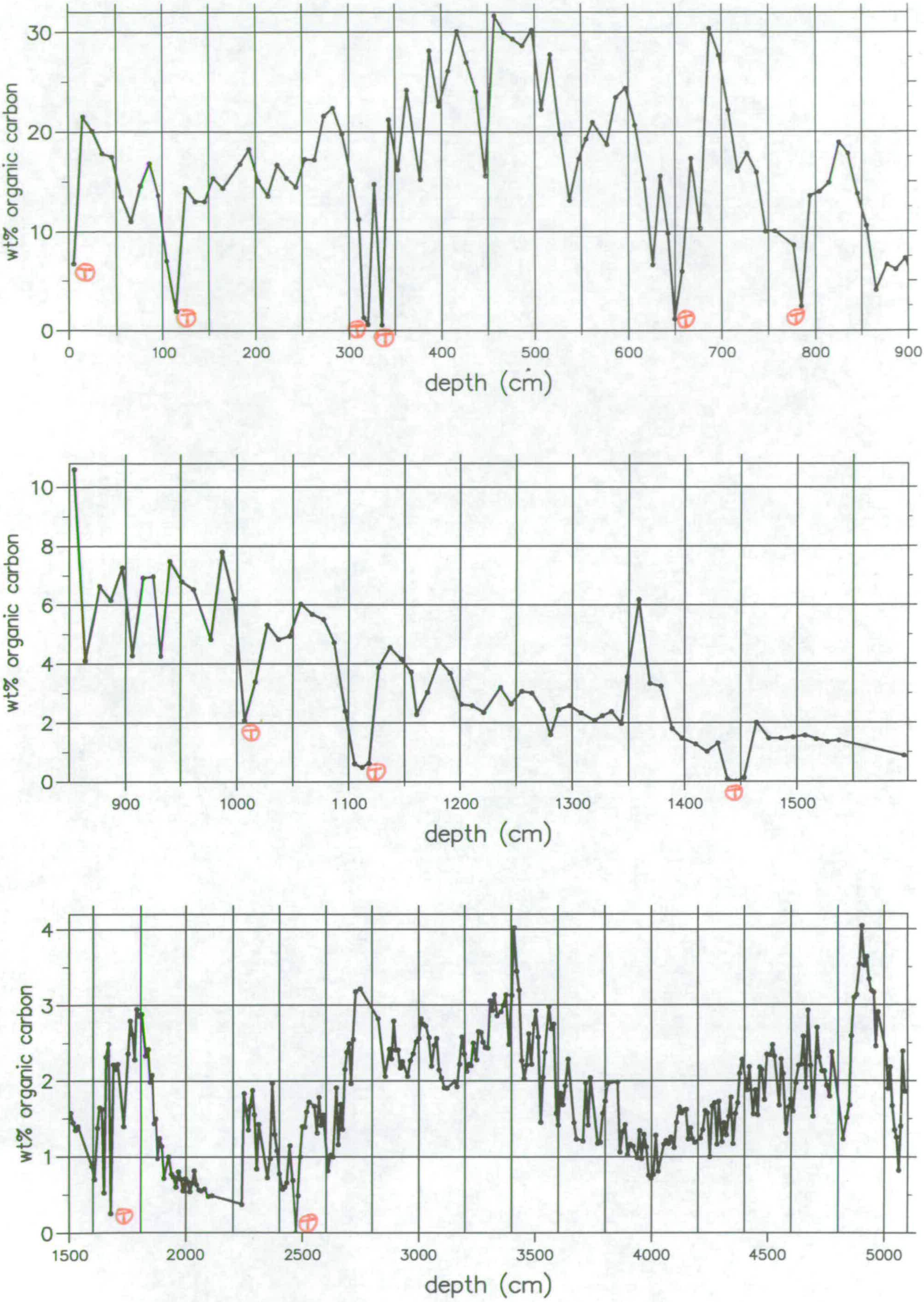


Fig. 4.2. Organic carbon content shown in more detail

(major tephra layers are marked by Ⓣ)

trend, however, appears to maintain high values of 20 to 30wt% C through to a third maximum at 460cm depth. From this point up to 125cm depth, organic carbon decreases gradually towards 15wt%. Following another tephra layer at 115cm, the organic carbon content begins to rise once more and the top of the core shows values of around 20wt% C. The uppermost sample is diluted by yet another tephra layer.

2) 860-1500cm. In the section from 1500 to 860cm a fairly steady upwards increase in organic carbon content is seen, perhaps levelling off above 1000cm. Two tephra layers of considerable thickness (>20cm) are found within the profile at 1450 and 1120cm. There also appears to be a pronounced organic-rich zone between 1390 and 1340cm. Here, organic carbon rises from a background value of 2wt% up to a brief maximum of 6wt%. This can be correlated with a number of dark brown horizons (each several cm thick) seen in the core section when freshly extruded.

3) 1500-5100cm. The organic carbon profile for the lower part of the core contains structural detail which is best examined on an expanded y-axis scale (Figs. 4.1. and 4.2.). The core record commences just before a minimum in organic carbon (1wt%) at 5050cm depth. Following this organic carbon rises sharply up to a 4wt% maximum at 4900cm depth, before dropping back to a 1wt% minimum over the next metre. Between 4700 and 3450cm there appears to be a broad cycle from values around 2.5wt% C to a minimum at 4000cm with <1wt% C values, and then back up to 2.5wt% C values over the next few metres. From 3450 to 3400cm organic carbon rises sharply to a brief maximum of 4wt%. This is of a similar magnitude to the maximum at 4900cm. From 3400 to 2700cm organic carbon remains relatively high at between 2 and 3wt% C. Values fluctuate between several maxima and minima, each lasting for one or two metres. At 2700cm the curve drops sharply to the 1wt% level and remains under 2wt% for the next 5 metres. A second sharp drop occurs at 2250cm where the visual record shows a slump unit and the beginning of a series of minerogenic turbidites. Here organic carbon content reaches some of its lowest values (0.5 to 1wt% C) in the whole record. Above 2000cm values start to rise slowly at first and then more steeply towards a maximum centred on 1800cm depth. The 3wt% organic carbon attained in this zone is obviously not as high as the previous maxima at 4900 and 3400cm. Elevated values continue for a further 150cm and then decline to values below 2wt% once more from 1650 to 1500cm.

Discussion

It should be remembered that the percentage concentration values presented in this study represent a closed data system and that one component can be diluted (show an apparent

decrease) merely by increase in the depositional rate of another component. Organic carbon content is affected by three basic factors:
1) productivity, 2) preservation, 3) dilution

1) PRODUCTIVITY The organic carbon content is both a reflection of organic productivity within the lake and of the productivity and supply of material from within the catchment zone. Within lakes, as in marine environments, increased productivity is generally considered to arise through increased nutrient availability (Birks, 1986; Tissot and Welte, 1984), and to a lesser extent by light or temperature increases, particularly in the productive epilimnetic zone. Lake productivity has generally been considered in terms of climatic factors, edaphic factors and morphometric factors (Carpenter, 1983). The effect of human activity might also be added to this list and is of major interest over more recent time scales. Each of these factors may have a direct or indirect effect upon nutrient availability. Increase in lake nutrient supply may come from external inputs (e.g. anthropogenic sources or changes in the catchment denudation or geology) or from recycling of the internal nutrient load (e.g. increased nutrient regeneration from the sediments). Terrestrial productivity in the lake catchment zone is influenced by edaphic factors and perhaps more directly by climatic factors as is often illustrated through the pollen record of vegetational change. This component of the organic matter also requires effective transportation into the lake to be included in the sediments.

2) PRESERVATION Organic matter is inherently unstable from a thermodynamic point of view and on average less than 0.1% of the amount produced in the biosphere survives into the geological record (Tissot and Welte, 1984). In the marine environment, the degradation of organic matter is widely recognised as approximating a 1st order rate process with respect to carbon concentration (Emerson and Hedges, 1988). In other words, under constant sedimentation conditions, the organic carbon content in the sediments should show an exponential decrease with depth. This simple model has been modified because organic matter consists of a mixture of components of differing reactivities. The more labile components should be consumed first and at a faster rate by microbial processes. More sophisticated models accommodate for these effects by evaluating different 1st order reactivities for the individual components or by modelling an overall decrease in organic matter reactivity with time (Middelburg, 1989). According to Lowe et. al. (1988), lacustrine organic matter typically consists of 30-60% humic and fulvic acids, 5-20% cellulose, 10-50% humin, <1% lipids and <1% amino acids. It would be expected that labile components such as the amino acids would be preferentially recycled at an early stage in the sediment pile and

that in deeper burial stages the remaining organics would undergo degradation at a slower rate as favourable substrates for microbial attack became less available.

The rate of organic matter degradation is affected by the quality of the organic matter, as mentioned, and by the availability of oxidants or electron acceptors (Gale et. al., 1992). The effects of physical mixing and bioturbation can also influence decomposition through aiding the movement of electron acceptors into the sediment zone. In a study of organic degradation in young lacustrine sediments by Avnimelech et. al. (1983) the authors found that the average rate constant was 4×10^{-3} to 24×10^{-3}. This translates into an organic matter 'half-life' of between 30 and 170 years. However, this rather rapid rate of decomposition was observed on sediment profiles encompassing the most recent few decades. Older sediment profiles representing time spans of up to 1000 years were found to have lower rate constants translating into organic matter 'half-lives' of hundreds or thousands of years. There are indeed wide variations in the rates calculated from the various laboratory and field studies made on lacustrine organic matter (e.g. Gale et. al., 1992; Ishiwatari and Uzaki, 1987). Emerson and Hedges (1988) attribute this wide range of degradation rates to the availability of different qualities of organic compound as substrates. Thus highly residual organic matter such as lignin has been shown to have an effective half-life of 400,000 years for its degradation in the sediments of Lake Biwa (Ishiwatari and Uzaki, 1987).

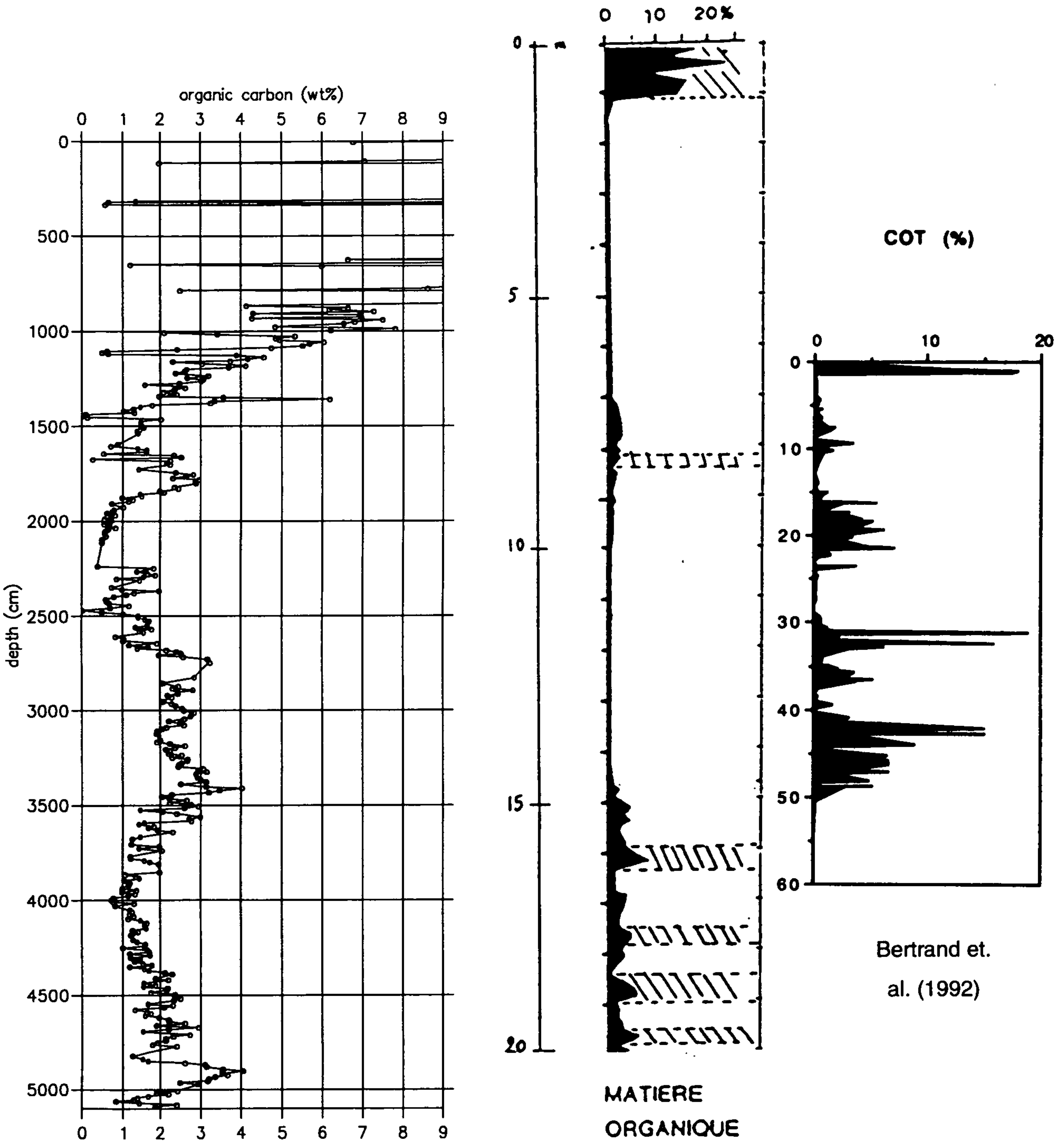
Although widely ranging values for organic decomposition exist, it is thought that in many organic lacustrine muds the majority of mineralisation takes place within the first few centimetres of the sediment-water interface (Herczeg, 1988; Lovley and Klug, 1986; Wersin, 1991). Below this acitve zone, decomposition may take place at a much slower rate until the onset of thermal decarboxylation (Tissot and Welte, 1984) at great burial depth. Part of this decrease in reactivity must be due to the early removal of the most labile components in the surface zone and part due to the diffusion-limited availability of oxidants from the overlying lake water. In many fine grained sediments oxygen, which is a particularly energetic decomposer of organic matter, only penetrates the upper few millimetres or centimetres of the sediment column (Berner, 1981). When oxygen has been consumed, organic decomposition continues through utilisation of a series of electron acceptors (Froelich et. al., 1979). These oxidants may also be consumed within the uppermost parts of the sediment due to limited replenishment by diffusion. Further degradation then takes place mainly by bacterial methanogenesis which does not require external sources of electron acceptors. It has been suggested that this mechanism of decomposition operates at a relatively slow rate (Pedersen and Calvert, 1990), but in some lacustrine settings vigorous methanogenesis has been documented during early diagenesis (Talbot and Kelts, 1986). It might be a reasonable assumption that this process is most effective in the top few decimetres of the sediment at Lago Grande di Monticchio and that, thereafter, the organic matter is permanently buried or suffers little further change.

Interpretations of long sedimentary records of organic carbon from lakes have tended to emphasise that the **primary control** over organic carbon content is productivity rather than preservation (Talbot and Johannessen, 1992; Brown, 1991; Meyers, 1989). Many of these records display shifts in organic content which are not constant in direction and occur over short stratigraphic intervals. If decomposition was the main control over carbon content then a systematic and monotonic decrease in organic carbon would be expected with depth. This is not seen in the case of the Monticchio record, where high organic carbon values persist for more than 700cm and then drop sharply over a short interval. The present organic carbon record will therefore be interpreted in terms of productivity being the driving force, although it is recognised that variations in the level of decomposition through time have had a secondary effect. The complication of changes in the degree of preservation (non-steady state diagenesis) is recognised by Meyers (1989) and requires additional information from organic geochemistry and optical examination if it is to be assessed.

3) DILUTION To properly evaluate the effects of dilution by other components on the organic carbon content requires accumulation rate data. From concentration data alone, it is not completely safe to state that the rise in organic carbon above 860cm depth is not merely the result of a sharp decrease in the input of minerogenic clastic material (and that the accumulation of organic carbon has in fact proceeded at a constant rate throughout!). Although accumulation rates cannot be calculated, it is possible to make reasoned interpretations using crude sedimentation estimates from the age models available and from ideas on the likely palaeoenvironment.

Interpretation

In the interpretation of the organic carbon profile, comparison is sought with similar lacustrine records, of which Lac du Bouchet (Fig. 4.3.) is considered the closest. Other long records of organic carbon content do exist, but their sampling resolution or dating control are relatively poor. From the study of Lac du Bouchet, Truze (1990) provides a model to explain the increases in organic carbon accumulation during periods such as the Holocene as compared with glacial times. This model will be applied to Lago Grande di Monticchio and it is summarised in cartoon form (Fig. 4.4a.) Briefly, an increase in terrestrial vegetation in response to a more humid or warmer climate causes the slopes of the crater catchment area to become stabilised. The ensuing reduction in erosional activity dilutes the amount of clastic



Truze (1990)

Bertrand et. al. (1992)

Fig. 4.3. Comparison of organic carbon profiles from Lac du Bouchet with the Monticchio record

deposition which may be seen as an *apparent* rise in organic carbon concentration. More importantly, weathering processes become dominant and increased nutrients leached from the soil lead to high productivity within the lake. Thirdly, as erosion and transportation declines the lake waters will stratify more easily due to reduced turbulence. Under elevated lacustrine productivity this could promote anoxic conditions in the hypolimnion zone (if present). This too could favour higher organic carbon contents in the sediments because preservation of deposited organic matter would be enhanced. The type of organic matter expected during these times would be mainly autochthonous and relatively labile. In contrast, during glacial periods erosional activity is more intense and organic productivity reduced. The type of organic matter predicted under these conditions would be highly degraded and consist mainly of resistant terrestrial debris. Truze considered that interstadial events, such as at 40,000 years B.P., represented 'intermediate environmental regimes' between these end members.

At Monticchio the rise in organic carbon immediately above 860cm most probably reflects such a response to a more humid and perhaps warmer climate. Discussion with other groups working on the record suggests that 860cm may be close to the start of the Holocene. This depth is comparable to that found for the Holocene boundary in an earlier palynological study (Watts, 1985) made on a core from the lake margins. Alternatively, it is possible that the actual transition is near 750cm. In this case, the area from 860 to 800cm might reflect a late-glacial interstadial (Allerød-Bølling event?), with an intervening period of climatic deterioration (Younger Dryas?) between 800cm and 750cm. Evidence of the Younger Dryas signal being observed in lake sediment geochemistry comes from southern Alaska (Engstrom et. al., 1990). Here a marked decrease in the sedimentary organic content and rise in mineral erosion (alumina content) are related to a 'pedogenic reversal' brought about by local vegetation changes. At Monticchio, such an interpretation requires further evidence from detailed palynology and independent dating controls for support.

A basic feature of the Holocene part of the record is the organic carbon maximum seen in the early part of this period from 700 to 400cm, followed by lower concentrations in the uppermost 400cm. As will be seen, the entire Holocene section is dominated by two components: organic matter and biogenic silica (i.e. biogenic material). The later Holocene appears to reflect a period when diatoms reach a dominant phase, whereas in the earlier part, other organisms such as green algae, blue green algae or terrestrial plants may have been greater contributors. This will be discussed more in relation to nutrient availability during the section on biogenic silica. Unfortunately, without accumulation rate data it is impossible to discriminate whether organic carbon deposition decreased or biogenic silica sedimentation increased during the upper 400cm. It is hoped that future results from varve analysis will make possible flux calculations.

The negative spikes in organic carbon content associated with tephra layers most probably reflect a simple dilution of the surrounding gyttja with inorganic material. Visual examination shows that the tephra layers are quite sharply defined and that organic rich sediments resume almost immediately above such catastrophic events. Previous studies (Mehringer et. al., 1977) have shown that tephra fall events occur over short time intervals of a few months or years and that secondary runoff from material deposited onto the catchment does not occur for long after this time. In some cases it has been found that the input of tephra has led to increased productivity (in particular of diatoms) as the lake recovers (Kurenkov, 1966). In Monticchio there are cases in the organic carbon record of a shift to higher concentrations above some tephra layers (e.g. at 1010cm depth), but some of these features might be connected with climatic improvement instead. Stimulation of productivity by the tephra may be outweighed by the already high productivity of the lake, especially during the Holocene. This subject will be returned to in Chap. 4b.

The organic carbon record from 860cm to the base of the sequence at 5100cm may be interpreted in alternative ways according to the two age models presented in Chap. 3. A central question regarding this interpretation is: 'Do we expect the Eemian interglacial to show similar levels of organic carbon as the Holocene?' If we examine the record from Lac du Bouchet it can be seen that in the 1987 20-metre core sequence (Fig. 4.3.) the Eemian contains only 5wt% carbon compared with over 15wt% carbon in the Holocene. Truze (1990) suggested that both greater degradation of the Eemian deposits and lower primary productivity during Eemian time might be responsible for the difference. Evidence from grain size measurements (Truze, 1990) had shown that clastic deposition was more active during this earlier interglacial and so the more turbid waters may have reduced the level of biological productivity. Preliminary results from the 1990 55-metre core sequence (Fig. 4.3.) show that organic carbon is again substantially lower during Eemian times as compared with the Holocene. However, at greater depth in this sequence, organic carbon levels as high as the Holocene occur once more. These are believed to be associated with earlier interglacial periods (T. Williams, pers. comm.).

With the young age interpretation, the more organic rich area between 2700 and 3400cm in Monticchio correlates with the zone around 10 metres depth in Lac du Bouchet (Fig. 4.3.) where a 40,000 year interstadial period is found. In Lac du Bouchet the organic carbon content at this time is slighly higher (2-3wt%) as compared with the surrounding glacial zones which contain <1wt% carbon. The lower organic rich area at 4900cm in Monticchio would correlate with the zone around 15 metres depth in the Bouchet profile. This is where organic content increases again, but not by as much as when the St Germain II interstadial/oxygen isotope stage 5a is reached. The last glacial maximum period in Monticchio might be considered to lie at around 2000cm where organic carbon values decrease to a <1wt% minimum for several metres. The area from here up to 860cm would thus be interpreted as the subsequent deglaciation leading towards the Holocene above. If this interpretation is correct, it appears that the last deglaciation contains an early period of enhanced productivity at 1800cm depth (soon after the glacial maximum) which is then followed by a drop to low productivity around 1500cm before productivity rises again towards the Holocene transition. This trend cannot be correlated with other known records which typically show a monotonic improvement during the last deglaciation.

The old alternative involves correlation of the more organic rich area between 2700 and 3400cm in Monticchio with the zone around 20 metres depth in Lac du Bouchet, i.e. the Eemian interglacial and St Germain I and II events (Fig. 4.3.). The area at 4900cm in Monticchio is correlated with the zone around 31 metres depth in Lac du Bouchet, i.e. a presumed interglacial at 240,000 years B.P. In this interpretation, the organic poor area at 2000cm in Monticchio is hypothesised to be the product of sustained dilution by a prolonged phase of clastic input to the system which may have involved factors other than climate (Chap. 4b). The actual last glacial maximum may be represented around 1500cm depth. This permits the organic carbon peak at 1800cm to be correlated with the 40,000 year interstadial seen at 10 metres depth in Lac du Bouchet.

The difficulty with this last interpretation is the need to account for the significantly lower organic carbon contents in the two previous interglacials. It is thought that the primary reason for this situation would have to be lower productivity during these times. It is considered unlikely that these zones once contained as much organic matter as the uppermost Holocene sediments and that degradation has reduced amounts to the present level below 4wt%. Also, for dilution effects to be responsible would require a very high sedimentation rate of clastic material in order to dilute the carbon flux. This seriously opposes the older age model which requires *low* sedimentation rates to reach back 100,000 years across only 20 metres. Although the involvement of the processes described by Truze (1990) is accepted as a cause for the broad differences between glacial and interglacial sedimentation at Monticchio, a new model (Fig. 4.4b.) is proposed at this stage. This is offered to provide a supplementary explanation of why organic productivity may have been lower during the last interglacial and in general during the earlier history of the lake.

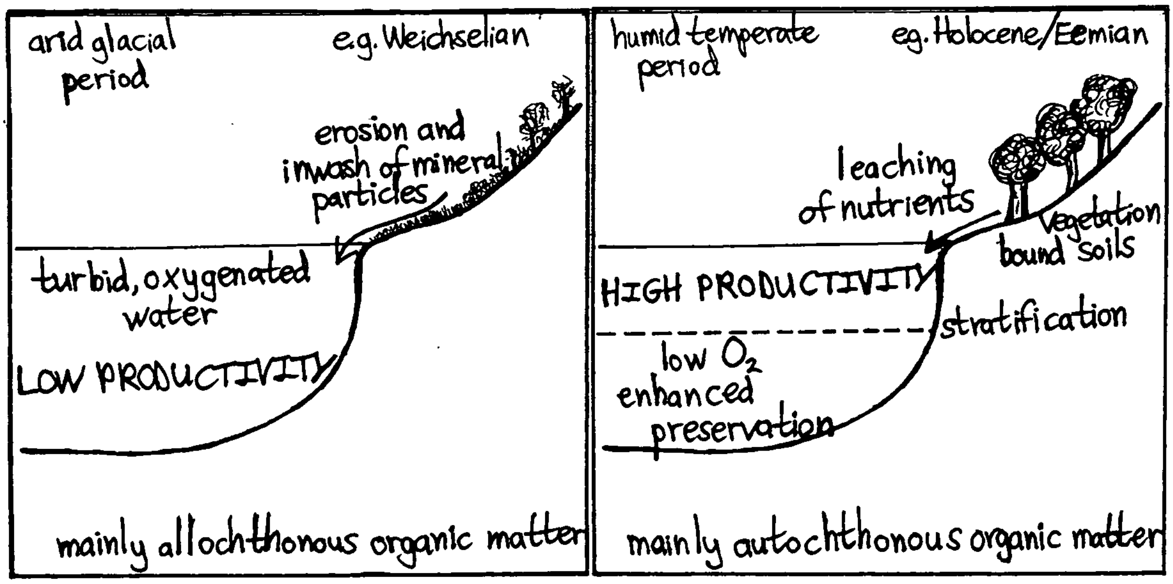


Fig. 4.4a. Model based on Truze (1990) involving the influence of changing catchment vegetation cover as a control over external nutrient input

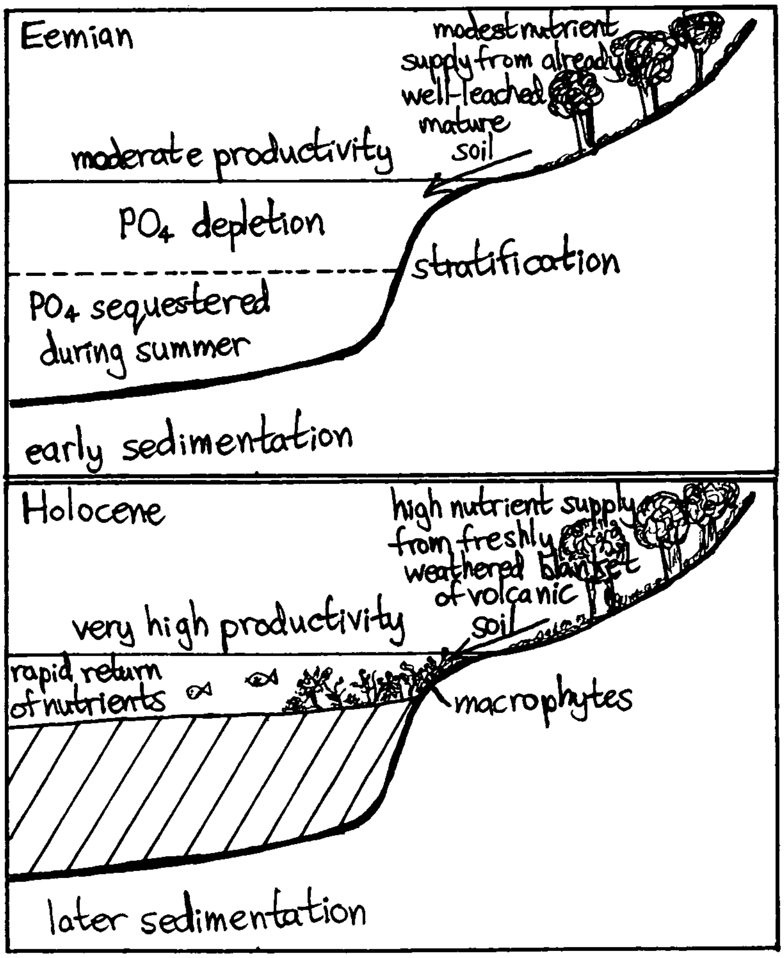


Fig. 4.4b. New model (based on the additional influences of tephra input and morphometric evolution) proposed to account for the difference between the Holocene and earlier interglacials

The new model incorporates the additional influences of A) evolution in lake morphometry (Binford et. al., 1983) and B) the effect of volcanic input upon edaphic conditions. This contrasts with Truze's model which only looks at climate as a driving force.

A) It is suggested that during its earlier history (before say 50,000 years B.P.) the lake was substantially deeper over its shelf area because it was less filled with sediments. This might have allowed a stratification regime to develop in which nutrients became sequestered into the hypolimnion for much of the productive summer period. This would limit further productivity in the water column and therefore cause less carbon to be fixed into the sediments. In contrast, gradual sediment accretion has led to a decrease in the depth of the shelf zone within the more recent history of the lake. Under these conditions, the epilimnion zone is in contact with most of the shelf surface and this could allow potential nutrient recycling to increase (Carpenter, 1983). Regeneration might be further enhanced by the spread of macrophytes across the shallow water zone. Recent observations show that pondweeds and other plants colonise large areas of the present lake (Chap. 2) and macrophyte vegetation is known to efficiently mobilise phosphorus through its roots and return it to the lake waters (Carpenter, 1981 and refs. therein). This change in nutrient supply and increase in productivity is associated with internal factors.

B) An external factor in the form of volcanic inputs may also play a role concerning the change in productivity at Monticchio. It is proposed that the earlier history of the lake was characterised by a relatively low number of tephra falls into the system. The soil in the catchment zone may have reached a mature and nutrient-depleted state over a previously long time interval. With very slow erosion of the crater slopes, new rock would not become exposed and available for leaching. Therefore the existing soil could be low in nutrients and, during the earlier interglacial periods, the increased weathering regime (according to the Truze model) would not be supplying the elements such as P and alkali metals into the lake in quantity. So, productivity would be relatively low. However, during the more recent history of the lake a greater number of tephras have been deposited onto both the lake and its watershed, especially in the record above 2500cm depth. This could have provided a thick blanket of 'fresh' mineral matter to the crater which became held in place by vegetation, permitting weathering and replenished inputs of external nutrients (c.f. Einarsson et. al., 1993). This would allow relatively high productivity to take place particularly in the sediments deposited above 2000cm depth.

This hypothesis is considered to provide a working explanation for the geochemical record in support of the old age model, but will require objective dating to prove or disprove. The new model (and the younger age interpretation) will be further discussed in relation to the rest of the geochemistry in subsequent sections. Next, some other biological aspects of the sediment geochemistry are dealt with.

C/N RATIO

C/N ratios can assist in defining the nature of the organic matter (Stuermer et. al., 1978). It should be noted that some authors present the weight C/N ratio, while others use atomic C/N ratios and sometimes the inverse (i.e. the N/C ratio) is shown. The atomic C/N ratio is equivalent to $1.16 \times C/N_{(\text{weight ratio})}$. Also the nitrogen, N, referred to may represent organic nitrogen or the more commonly determined total nitrogen content of the sample. In this study, C/N ratios refer to the weight ratios of organic carbon to total nitrogen in the sample.

The C/N ratios in the Monticchio core (Fig. 4.5.) show fluctuations between zero and >17, although most samples lie between values of 5 and 15. From 5100cm to 3500cm there is a broad correspondence between high C/N and high organic carbon values. C/N ratios decrease from 12.5 at 4900cm to 5 at the organic carbon minimum around 4000cm. Above this depth, C/N rises to its highest values in the entire profile from 3500 to 3250cm. This contrasts somewhat with the more subdued organic carbon maximum in the same zone. After 3250cm, the ratio drops back to below 10 as 3000cm is approached, while maintaining a good correlation with the organic carbon profile. Another minimum (C/N=5) is reached at 2000cm where some of the lowest organic carbon concentrations occur. This is followed by a maximum of 10 or 11 in the 1850 to 1600cm zone, again correlating well with elevated organic carbon. The area of the profile between 1600 and 1150cm is particularly noisy, but appears to begin with a minimum (C/N<6) up to 1400cm followed by a maximum (C/N 7-12). Values fall back to <5 at 1100cm and then rise progressively towards the presumed glacial-Holocene boundary. A maximum C/N ratio of 10 is reached at 850cm. This is followed by a downturn over the next metre which correlates with the possible Younger Dryas signal mentioned previously. Above 750cm the ratio rises back from <5 to 10. The remainder of the Holocene is characterised by fairly constant values of 9-12, although the uppermost 150cm shows generally higher values than the rest of this section. As with the organic carbon record, tephra-rich samples impose negative spikes on the overall trend. Indeed, most of the samples displaying C/N<5 are ones in which there is a significant tephra component.

Discussion

The C/N ratio may be a reflection of both the source(s) of the organic matter and its level of diagenesis. A table compiled with data from Muller (1977) and Bremner (1967) is presented

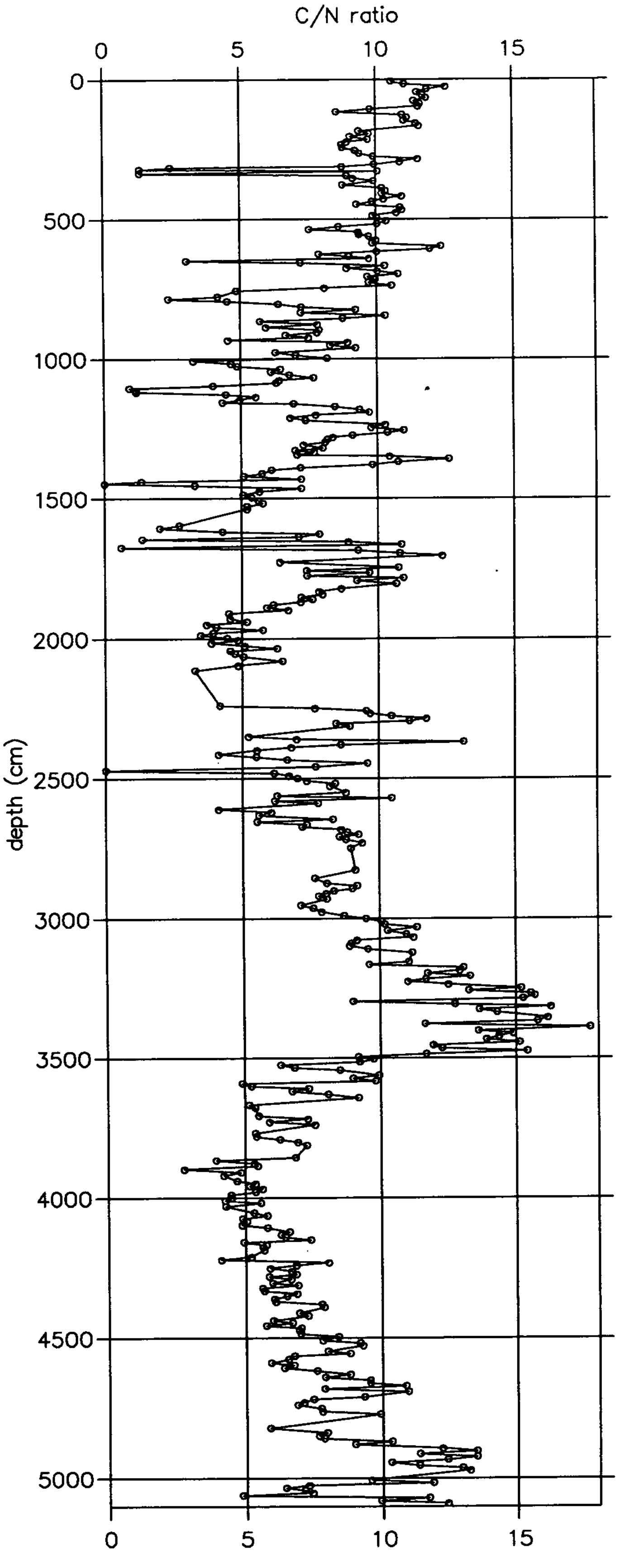


Fig. 4.5. Carbon/nitrogen (C/N) ratio
(N here refers to total nitrogen)

to show some of the range in values for organic matter and for soils (Table 4.1.). Essentially, organisms have different C/N ratios according to the amounts of protein that they contain. A major difference exists between algae or lower organisms which contain high amounts of protein (giving C/N ratios of 5 to 8) and the more cellulose-rich terrestrial plants which typically have C/N ratios greater than 15.

component	**C/N ratio**
proteins	3.0
zooplankton	5.4-5.9
bacteria	4.0-5.0
blue-green algae	6.5
diatoms	5.5-7.5
terrestrial plants	15.0-100.0
most soils	9.0-22.0

Table 4.1. Average C/N ratios associated with different sedimentary components.

It can be seen that some of the groups in Table 4.1. display considerable overlap in values. This precludes a detailed reconstruction being made from bulk geochemical data and it may only be possible to distinguish between the relative contributions of higher versus lower plant groups.

The effects of diagenesis are generally accepted as leading to an increase in the C/N ratio of the remaining sedimentary organic matter. This is found both in the marine environment (Stevenson and Cheng, 1972) and in lake sediments from laboratory (Gale et. al., 1992) and field (Herczeg, 1988; Kuivila, 1984) studies. An illustration is provided by a sedimentary profile from a small lake in New York State (Fig. 4.6.). Here the C/N ratio is seen to increase from below 11 in the surface sediments to around 13 at 5cm depth. Beyond 5cm, however, the ratio remains more or less constant. This preferential loss of the nitrogen-rich fraction of organic matter is also evidenced from sediment porewater studies. Kuivila (1984) found that the C/N ratio of the organic matter *being decomposed* was 3.9 at 7cm depth, but rose to 14.7 at 53cm depth in the sediments of Lake Washington. Most studies show that after intial

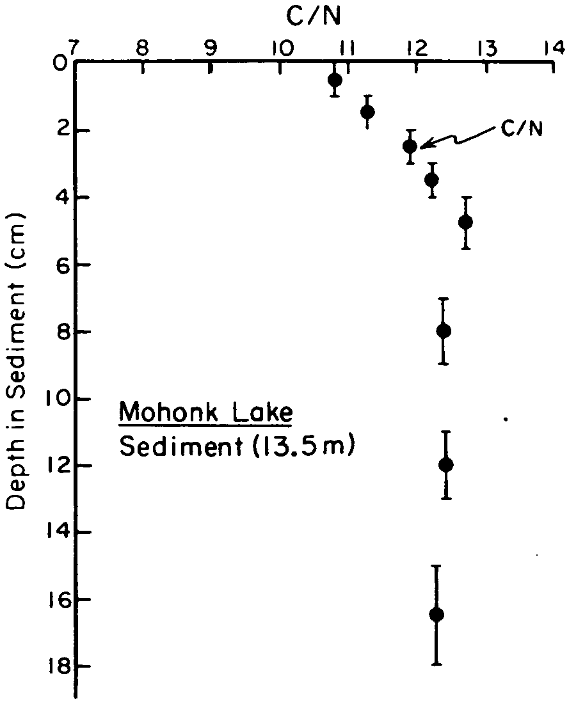


Fig. 4.6. Carbon/nitrogen ratio profile from sediments of Mohonk Lake (modified from Herczeg, 1988).

preferential losses in a zone of active diagenesis, the deeper sedimentary organic matter ceases to become nitrogen depleted (Binford et. al., 1983). These conditions of long term stability at depth should allow some indication of the primary source components to be retained. However, it is worth noting that some studies from the marine record suggest a continued change at greater depths (Stevenson and Cheng, 1972), perhaps due to non-biological reactions.

Unfortunately, a reconstruction of the primary organic sources (with a diagenetic overprint that can be estimated for) from the sediment record may be complicated by the retention of released nitrogen onto clay minerals (Lew, 1981). This phenomena will not affect studies where *organic nitrogen* has been analysed for, but could represent a problem for organic carbon/total nitrogen ratios, particularly in organic-poor sediments. When low amonts of organic matter are present, an appreciable percentage of the total nitrogen may be inorganic leading to erroneously low C/N values. Muller (1977) also recognised the possiblity that organic nitrogen compounds released by diagenesis could be preferentially retained by adsorption onto clay minerals. It was suggested that montmorillonite in particular might protect these compounds which would otherwise be lost from the sediments.

In a palaeoenvironmental reconstruction we would mainly like to use the C/N ratio as an indicator of organic matter sources. Most results from long lacustrine records have been able to make associations with changing source inputs (Meyers, 1989; Meyers et. al., 1993; Talbot and Johannessen, 1992), but are only able to go as far as distinguishing relative changes at the terrestrial versus lower aquatic plant level.

Interpretation

In the interpretation of the Monticchio record it is thought that early diagenetic losses of nitrogenous organic matter could be tenuously associated with the rising C/N trend over the top 25cm of the core (Fig. 4.5.), but that the majority of the record may be shaped by the C/N ratios of organic (and inorganic) source contributions. Under the present limnological conditions it is likely that most of the early regeneration of nitrogenous organic matter occurs in the topmost unconsolidated sediment layers or in the water column, both above the attention of the core record studied here.

The Holocene C/N ratios are generally close to 10 and probably reflect a mixture of terrestrial components with a major aquatic lower plant component. The relative constancy in ratio over perhaps 10,000 years of sedimentation suggests that the period has not experienced any fundamental changes in the basic organic mixture. The higher values around 12 in the upper 150cm of the profile could be associated with an increase in aquatic macrophytes (high C/N plants) across the lake shelf. It is possible that the presence of their root systems could also have increased nitrogen loss from these sediments.

During the Holocene and at earlier times, tephra samples are seen to drag the C/N ratio to very low values. Although tephra inputs may sometimes stimulate blooms of *lower plants* (e.g. diatoms) the ratios associated with these samples are below the range of known organic sources. However, if the geochemistry of typical catchment area rocks is examined (Table 2.1.) it can be seen that this primary inorganic material contains virtually no carbon, but up to 0.07wt% nitrogen. This is an unusually high nitrogen content for an igneous rock, normal values being below 0.01wt% nitrogen (Stevenson, 1962). According to Stevenson (1962), the nitrogen content of igneous rocks is a function of the type and amount of silicate minerals present and the amount of ammonium available for fixation during the existence of the mineral. In this case ammonium nitrogen is probably substituting in place of K in the lattice of feldspar or feldspathoid minerals, and it has been shown in Chap. 2 that many of the volcanic rocks in this region are enriched in volatiles, possibly from evaporite assimilation. As a result, the local volcanic material has an effective C/N ratio close to zero and a large amount of this component in the sediment mixture could account for the very low C/N ratios in the core profile.

The zone between 500 and 2000cm, encompassing the last glacial transition, is shown in more detail in Fig. 4.7. From 750 to 1150cm depth the C/N ratio decreases from 10 towards 5. This general trend also contains a sharp drop to low values in the 750cm to 800cm zone which may equate with the Younger Dryas period. These trends towards values as low as 5 suggest that diatoms or algae have become the dominant source of organic matter. Comparison with the organic carbon profile (Fig. 4.7.) shows that a positive correlation exists between the two parameters. Assuming that dilution and diagenetic effects are of secondary importance, this suggests that the amount of organic matter supplied by terrestrial vegetation and/or aquatic macrophytes has decreased significantly while the input from planktonic productivity has decreased at a lower rate or maintained its level. In the possible Younger Dryas period this would suggest a sensitive response to climate from productivity in the terrestrial/catchment vegetation zone, but a lower response from productivity changes within the lake.

After interruption by a tephra layer around 1100cm depth, the zone between 1150 and 1400cm appears to indicate a relative increase in the contibution of terrestrial plant material. This is set against a background of declining organic carbon content (Fig. 4.7.) and is interpreted as reflecting decreased organic input from both the catchment vegetation **and** from plankton within the lake due to declining climatic conditions and nutrient availability. High areas of C/N, especially around 1360cm depth, suggest certain periods of increased terrestrial organic matter input or aquatic macrophyte contributions.

Between 1400 and 1600cm depth, organic carbon values are reduced to below 2wt% C and the C/N ratio is around 5 suggesting a limited contribution from lacustrine plankton and virtually no contribution from higher plant matter to the sediment organic matter. A return to higher organic carbon content and C/N ratios up to 12 occurs between 1600 and 1800cm depth and suggests that the input of terrestrial vegetation and perhaps also the productivity within the lake has increased again in response to improved climate/nutrient supply. This is followed by the zone around 2000cm where high clastic deposition dominates the sediments. The organic carbon and C/N values suggest an organic sedimentation similar to that between 1400 and 1600cm, although the possible effect of inorganic nitrogen on the C/N ratio of these organic-poor sediments needs to be considered. The possibility of inorganic

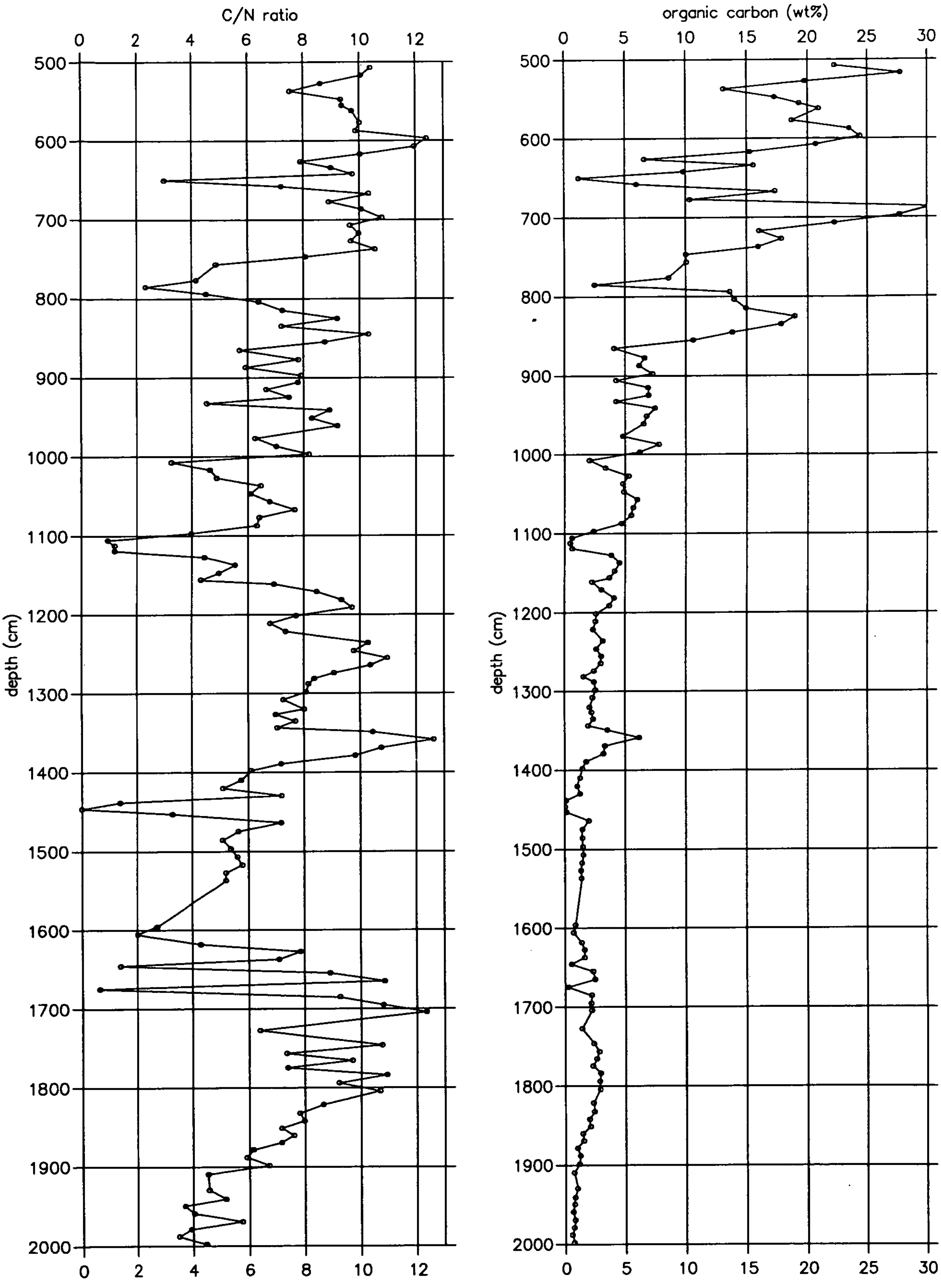


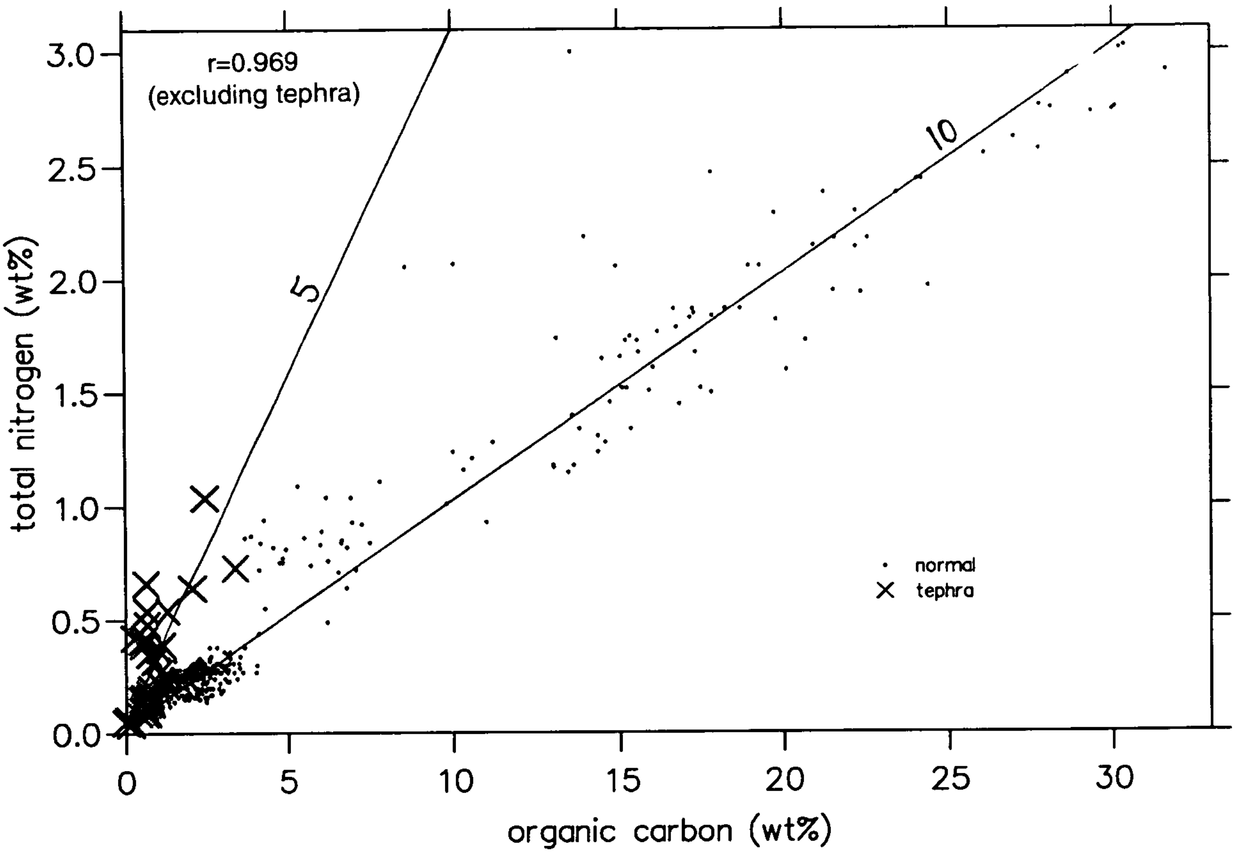
Fig. 4.7. Comparison of C/N ratio and organic carbon content for the zone between 500 and 2000cm depth

nitrogen affecting the sediments which contain <2wt% organic carbon will be dealt with in the following paragraphs, but for the moment the interpretations are based on C/N ratio principally reflecting the organic matter C/N ratio.

The remainder of the profile (Fig. 4.5.) contains two important maxima in C/N ratio at 3200 to 3500cm depth and at 4900cm. These periods have been suggested as interglacials according to the old age interpretation or otherwise interstadials, and organic carbon content is generally elevated. Both lacustrine and catchment productivity were probably somewhat higher during these times, with the relative increase in higher plant sedimentation dominating the C/N signal. The lower C/N and organic carbon values outside these zones reflect gradients towards reduced contributions of terrestrial organic matter and the dominance of planktonic matter components. It is interesting to note that if the older age model is correct, the Eemian contains a strong signal from high C/N ratios, while the predicted St Germain I and II interstadial zones between 2700 and 3200cm show relatively low or intermediate values.

The sediments in lower parts of the Monticchio profile show some correlation between C/N ratio and the organic carbon content. Such a relationship was found in the Lake District area by Mackereth (1966) and attributed to the increasingly significant contibution of mineral NH_4^+ under conditions of low organic matter abundance. Analysis of the local glacial clays showed them to contain 0.20wt% nitrogen -an extremely high value. The presence of this component was held responsible for the artificially low C/N ratios in some sediments. It is to be wondered whether the effect of high levels of inorganic nitrogen may be responsible for the often low glacial C/N ratios (<7) in the Monticchio record and if the removal of this effect might perhaps shift the ratios in these zones to much higher values.

In a plot of total nitrogen against organic carbon (Fig. 4.8.) it can be seen that the two parameters are strongly correlated suggesting that the nitrogen content is mainly associated with organic matter. Virtually all of the samples fall within fields representing C/N ratios of 5 to 15. The main exceptions to this are tephra layers which have been marked separately on the diagram. These *do* contain significant amounts of inorganic nitrogen and display sharp excursions to low C/N. In contrast, the majority of samples in the core profile lay above a minimum 'threshold ratio' of 5 and remain separate from the extreme tephra values. It is considered reasonable that C/N ratios as low as 5 could be related to mainly or exclusively organic nitrogen components. A further consideration is the fact that the 'best-fit' line intercepts the y-axis at around 0.05wt% nitrogen which could represent a reasonable maximum for the fixed level of organic nitrogen present in most of these sediments. This



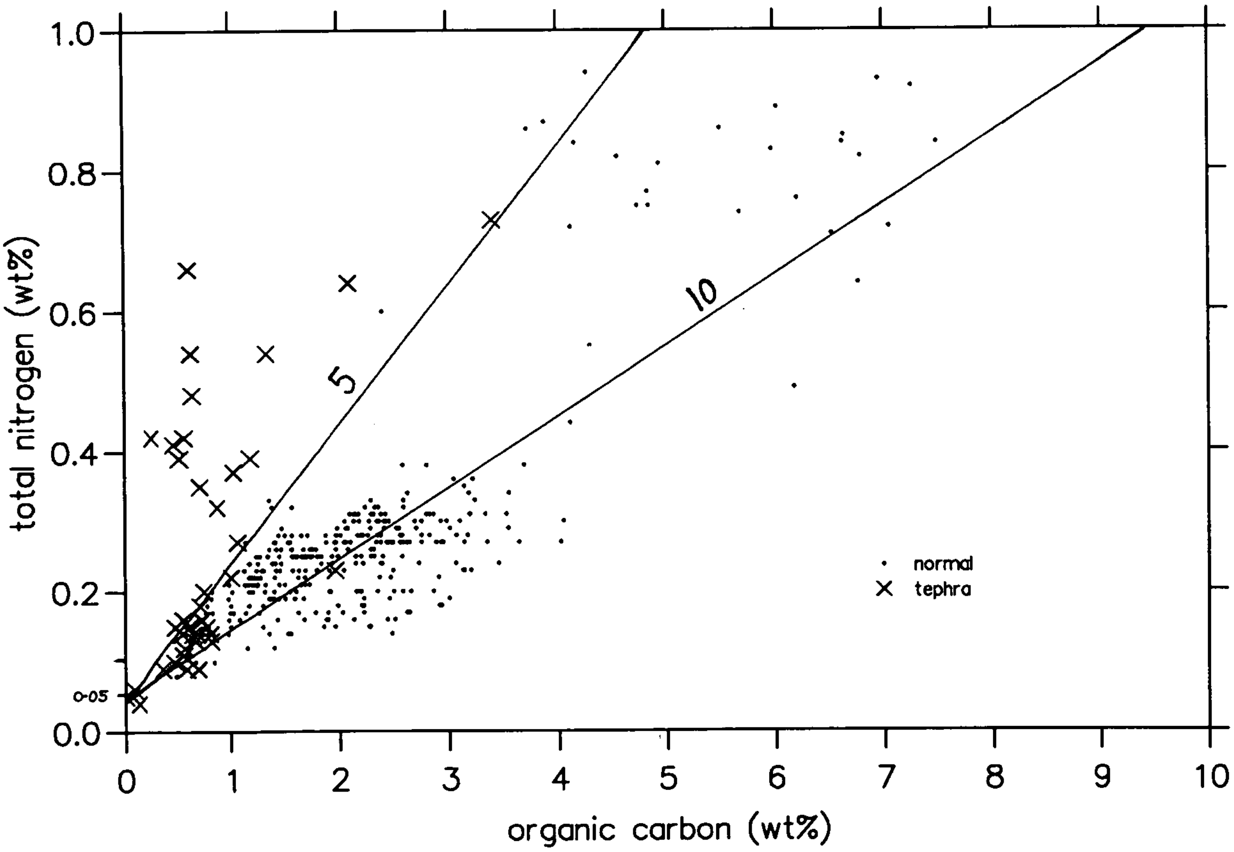
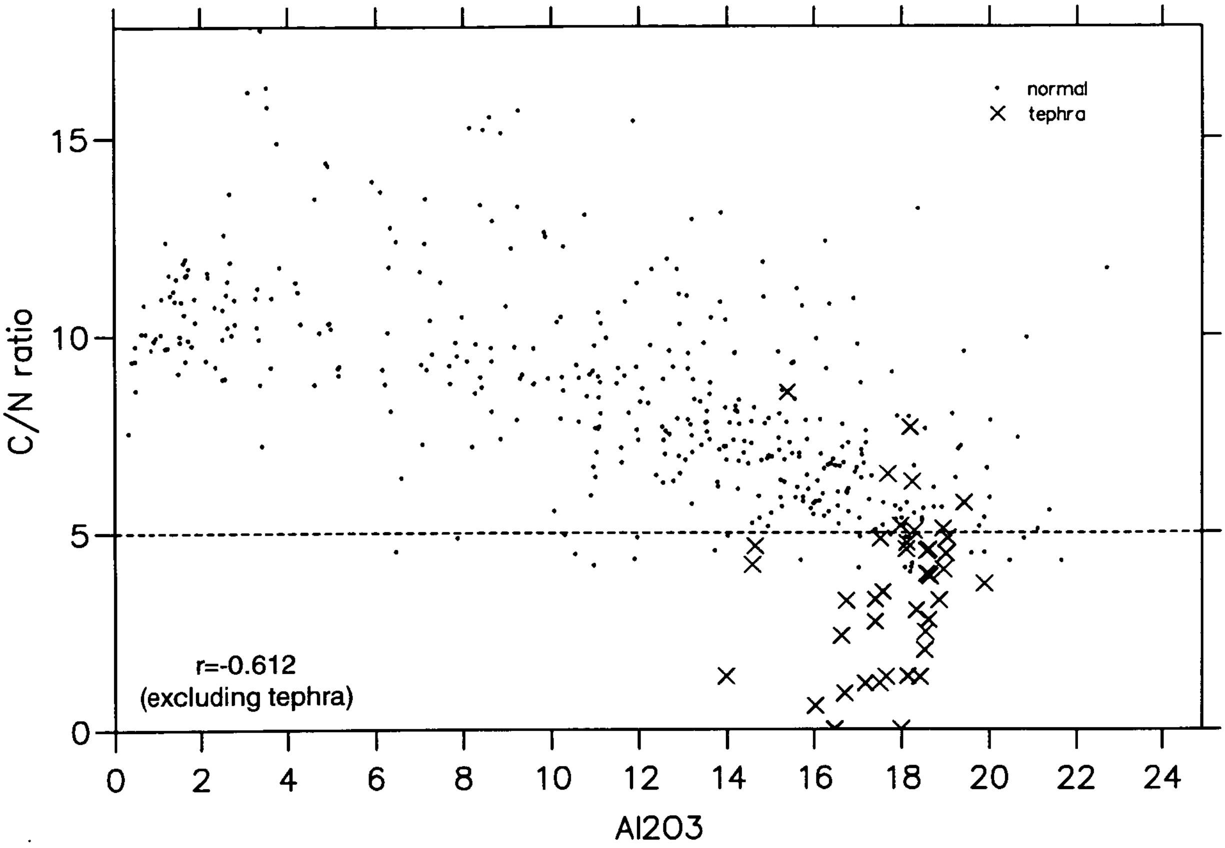


Fig. 4.8. Total nitrogen plotted against organic carbon content (normal and tephra rich samples are distinguished)



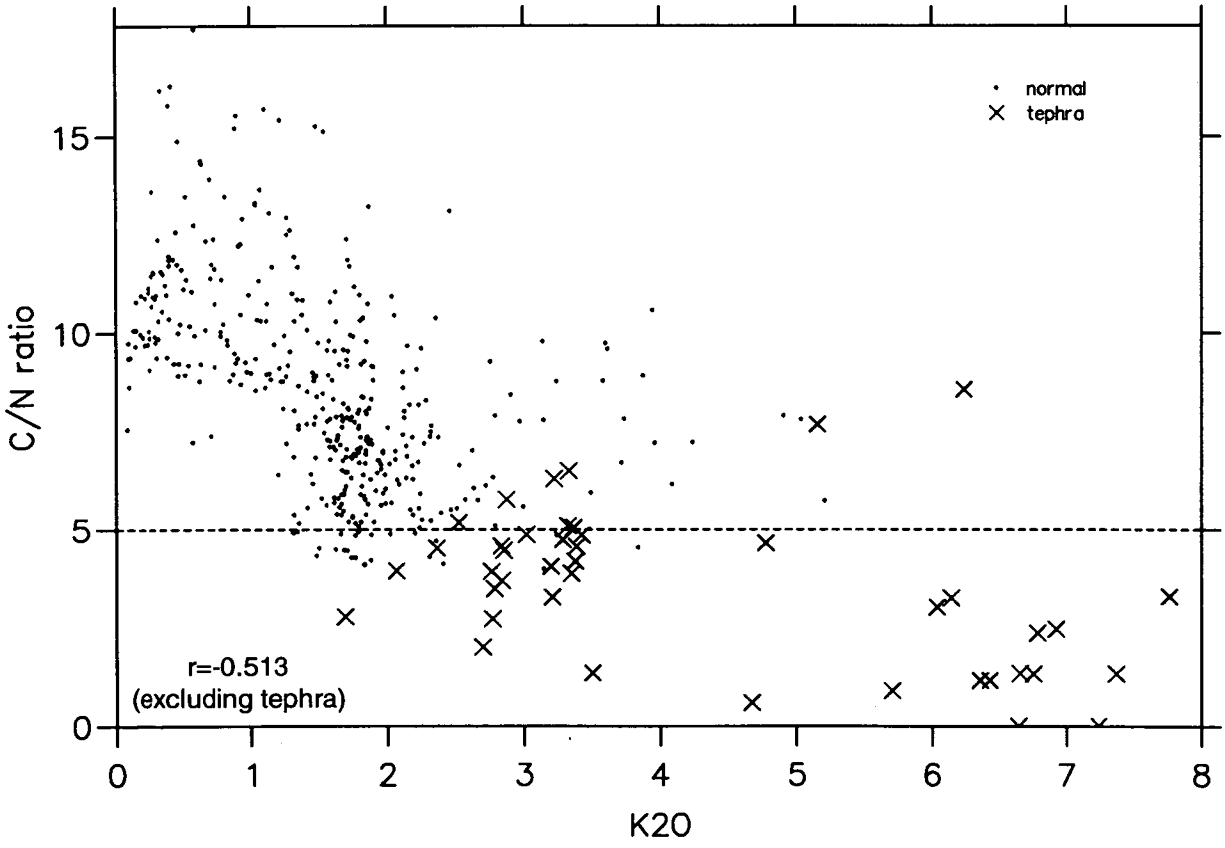


Fig. 4.9. C/N ratio plotted against alumina (above) and K_2O content (below)
(normal and tephra rich samples are distinguished)

value is in accordance with lake and marine studies by Kemp and Mudrochova (1972), Stevenson and Cheng (1972), Muller (1977), Lew(1981) and Talbot and Johannessen (1992) who all find that the level of sedimentary inorganic nitrogen to be below 0.05wt%. If this figure is then removed from total nitrogen values during high-glacial times (e.g. at 4000cm depth) it is found that an adjusted C/N ratio rises from 5 to 6.7. This is still very much lower than the adjacent interglacial or interstadial zones which have ratios of 10 or more.

In a plot of C/N ratio against mineral content indicators such as aluminium or potassium (Fig. 4.9.) the tephra layers are again seen to stand out with their exceptionally low C/N ratios and high mineral contents. Muller (1977) found a strong positive correlation between inorganic nitrogen content and the concentration of mineral indicators. If the presence of appreciable mineral-associated nitrogen was influencing the C/N ratios in Monticchio it might be expected that a plot of C/N ratio against mineral indicators would show a strong negative correlation. It should be remembered that, as a variable, C/N ratio is dependent on both inorganic nitrogen contributions and on the strict C/N ratio of the organic matter, and that the fundamentals driving sedimentation may influence both simultaneously. The scatter plots of C/N ratio against aluminium and potassium show only weak to moderate negative correlations amongst the body of samples, and this also suggests that inorganic nitrogen is not a primary factor of influence to the C/N ratios. However its increased presence could enhance C/N to *slightly* lower ratios during mineral-rich glacial periods of deposition. A possible reason for the limited presence of inoganic nitrogen may be the low abundance of suitable host phases such as illite or montmorillonite over large parts of the core (see Chap. 4b).

In summary, the sediment C/N ratios are not thought to be primarily influenced by inorganic nitrogen contributions with the exception of tephra inputs and high clastic sedimentation by turbidites. Therefore the C/N ratios may largely reflect the organic matter composition. Nevertheless, it may be possible that the sediments have experienced some lowering of the C/N ratio during organic matter diagenesis. This opposes the normally encountered increase in C/N ratio discussed earlier, but Kemp and Mudrochova (1972) associated increased organic nitrogen contributions with the complexing of amino-compounds to newly formed humic materials. This process was thought to be most effective during periods of slow sedimentation when bacterial populations would have more time to degrade the sediment organic matter. Further investigation into characterising the phases with which N is associated (e.g. by selective extraction procedures) would seem worthwhile in order to reliably interpret the C/N record.

BIOGENIC SILICA

Like organic carbon, biogenic silica offers a guide to past biological productivity. But while the former variable is related to the general level of organic production within and surrounding the lake, biogenic silica reflects a specific portion of lacustrine production -in general the abundance of diatoms. Although microscopic examination reveals the presence of other siliceous organisms in the Monticchio sediments, such as chrysophyte cysts and sponge spicules (Zolitschka, unpubl. work), the dominant siliceous organisms here are diatoms. This is illustrated by S.E.M. photographs taken at 1750 and 3410cm depth within the core (Plate 6.) which show the large quantities of diatom valves that often occur. In fact the Monticchio sediments are particularly rich in this component over many depth intervals, probably a reflection of the lake's volcanic setting (Martin et. al., 1992; Jones and Bowser, 1978). Pyroclastic minerals are known to be subject to greater dissolution and alteration than normal catchment rocks and large amounts of silica can be derived through weathering processes to stimulate high diatom productivity. A great deal of information may be derived from the study of the diatoms in their own right (Battarbee, 1986; Dixit et. al., 1992), but this study will look just at biogenic silica as a proxy indicator of absolute diatom concentrations. It may be the case that the biogenic silica record has experienced better preservation than the organic carbon record allowing a clearer signal of past productivity. The biogenic silica record might also provide complimentary information on conditions such as nutrient levels through its contrasts with total organic carbon.

During the determination of actual biogenic silica (Appendix 1) it was found that the early results correlated extremely well with a normative model for biogenic silica calculated from the XRF major element data:

$$\text{biogenic silica}=SiO_2-2.8*Al_2O_3$$

This calculation is similar to that employed by Bostrom et. al. (1972) and assumes that total silica is composed of a biogenic component and an aluminosilicate+quartz component. The factor of 2.8 selected is lower than an often quoted 'average shale' silica:alumina ratio of 3.4 (Turekian & Wedepohl, 1961), but fits the more aluminous sediment type from these cores better. As the actual measurement of biogenic silica is time consuming it was decided to continue with a smaller number of selected samples below 970cm in order to verify the accuracy of the XRF estimation model. Comparison of the two curves (Fig. 4.10.) shows that below 970cm some discrepancy occurs and negative estimations of biogenic silica are seen at 2000cm and 4000cm depth. This must be due to changes in the silica:alumina ratio of the

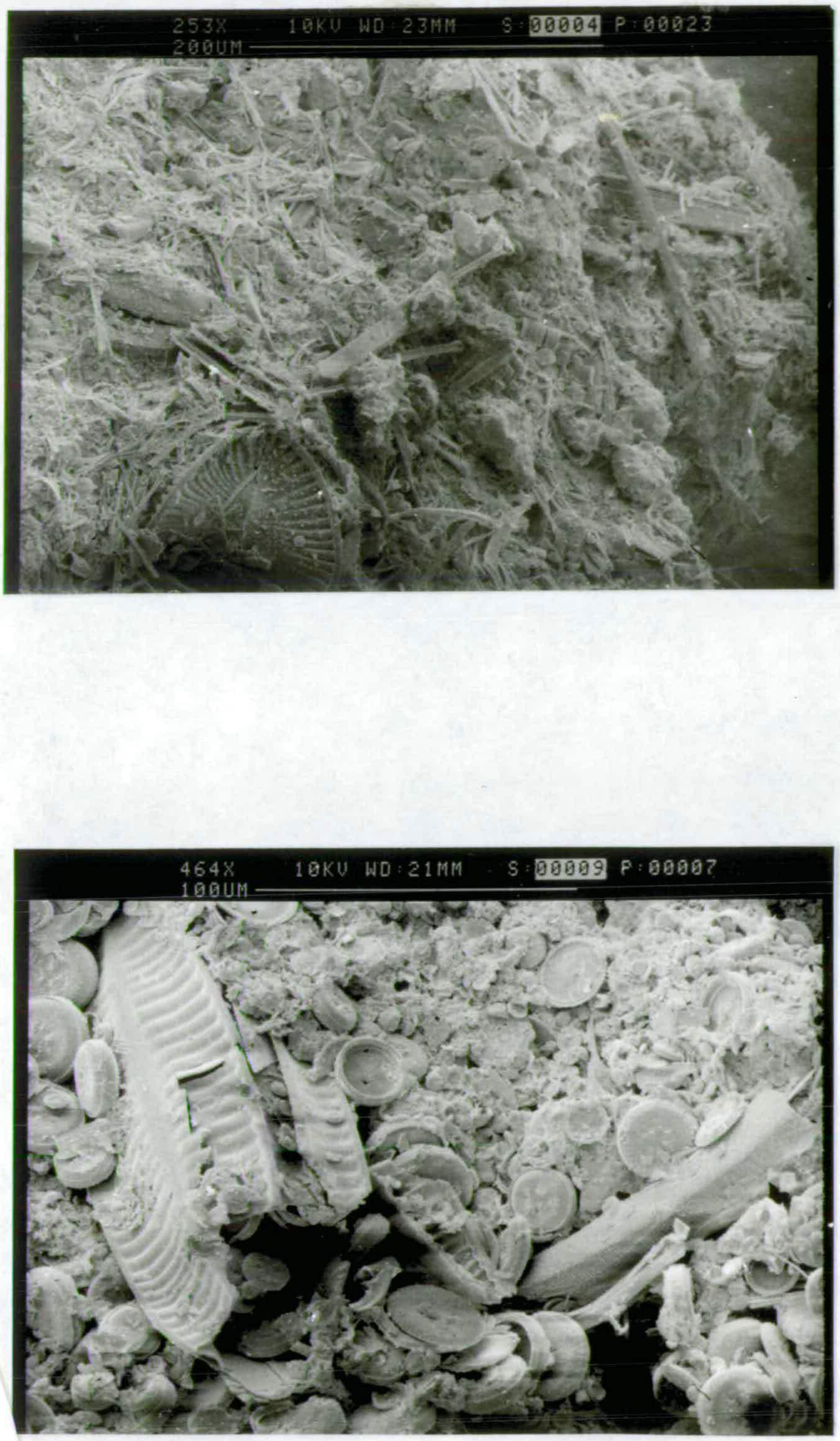


Plate SEM photographs of diatom remains from 1750cm (above) and 3410cm (below) in the profile.

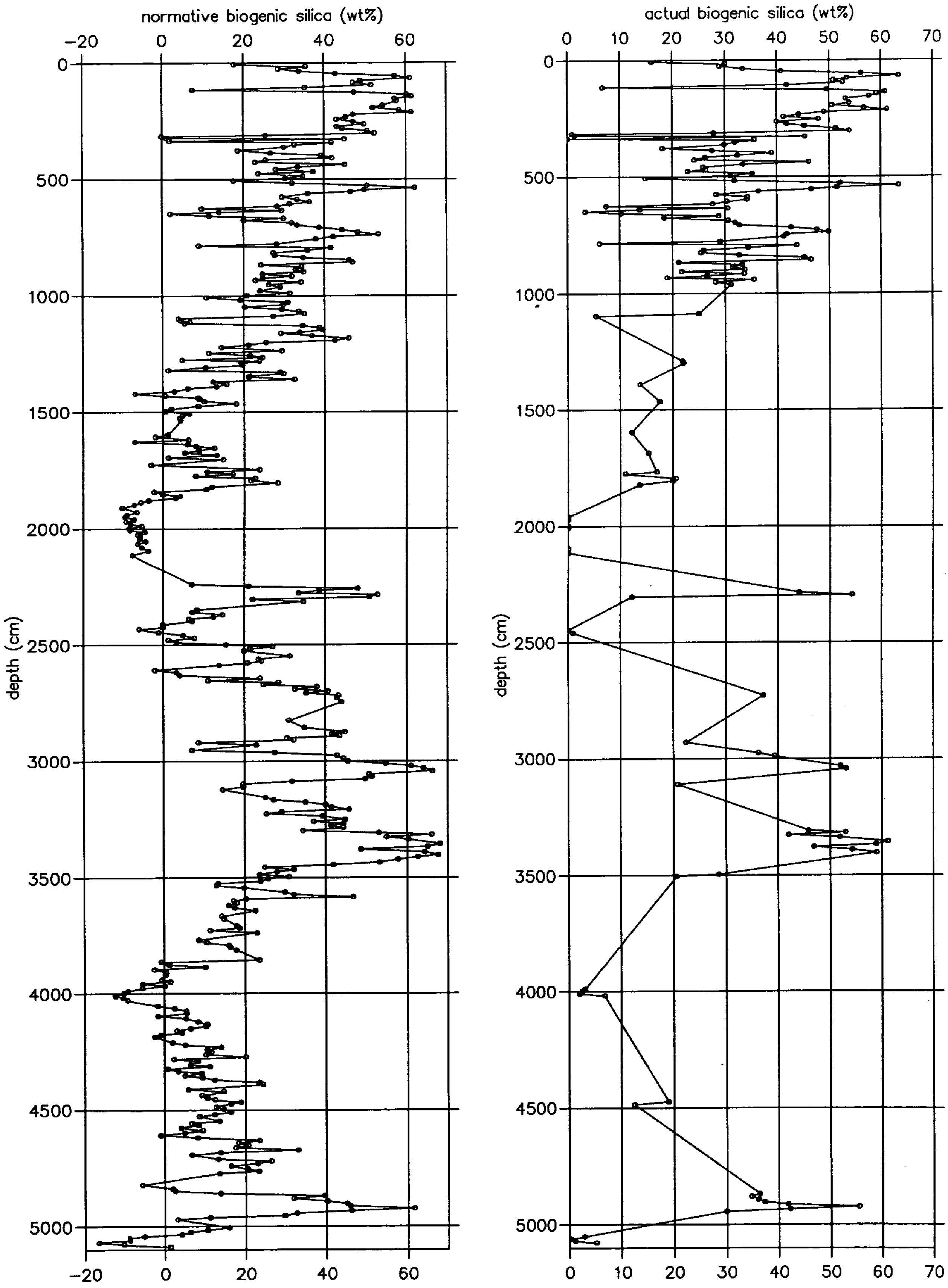


Fig. 4.10. Biogenic silica content (normative model and actual measured values)

non-biogenic sediment fraction as a result of changes in aeolian dust input, tephra input and local weathering processes which all contribute to the sediment mixture. Previous attempts to improve the normative technique have applied well-constrained mineralogical modelling and included additional parameters in the normative calculation (e.g. Leinen, 1977). However, for the Monticchio record, the more simple normative model above offers an adequate high resolution semi-quantitative guide to the large scale variations that occur in biogenic silica content. This can be used in conjunction with the more limited profile of actual biogenic silica concentrations to pin down absolute values.

If the biogenic silica profile is viewed as a whole (Fig. 4.10.), the lower part of the profile (below 2000cm depth) shows broadly comparable trends to organic carbon content (c.f. Fig. 4.1.), but the signal from the biogenic silica record is much more accentuated. For example, the zone around 3400cm which may represent the Eemian interglacial (according to the old age model) shows biogenic silica contents of 60wt%, while values drop to effectively zero at 2000cm depth. Microscopic examination has shown that diatoms *are* present throughout the entire profile, although at 2000cm and 4000cm they occur in very low numbers (Zolitschka, unpubl. work). If the old age model is applied, it is seen that the stage 7 interglacial, the Eemian and the St Germain I interstadial are all characterised by very high levels of biogenic silica reaching over 50wt% in value, but that the suggested St Germain II period at 2700cm depth contains a noticeably lower content around 40wt% SiO_2. The biogenic silica record also appears to pick out more clearly possible interstadial events at 2600cm and 2300cm depth. The latter event again records very high levels of biogenic silica over 50wt%.

In the upper part of the profile the biogenic silica content increases from 0 towards 30wt% between 2000 and 1000cm depth (Fig. 4.11.). This parallels the broad trend shown by organic carbon (Fig. 4.11.), although the climatic improvement suggested by the elevated organic carbon levels between 1600 and 1800cm appears more subdued in the biogenic silica record than might be expected. Above 1000cm the biogenic silica content varies more independently with regard to organic carbon content and the two parameters only correlate closely where tephra layers dilute both with high amounts of clastic material. From Fig 4.11. it is clear that much of the upper 700 to 1000cm of the Monticchio record is dominated by organic matter and biogenic silica (diatom) constituents and that clastic mineral matter only represents a small contribution outside the areas of high tephra input.

From 1000 to 780cm depth biogenic silica content remains around 30wt% with two fluctuations towards higher values over 40wt%. The previously suggested Younger Dryas zone does not suffer a significant decline in biogenic silica outside the brief influence of a

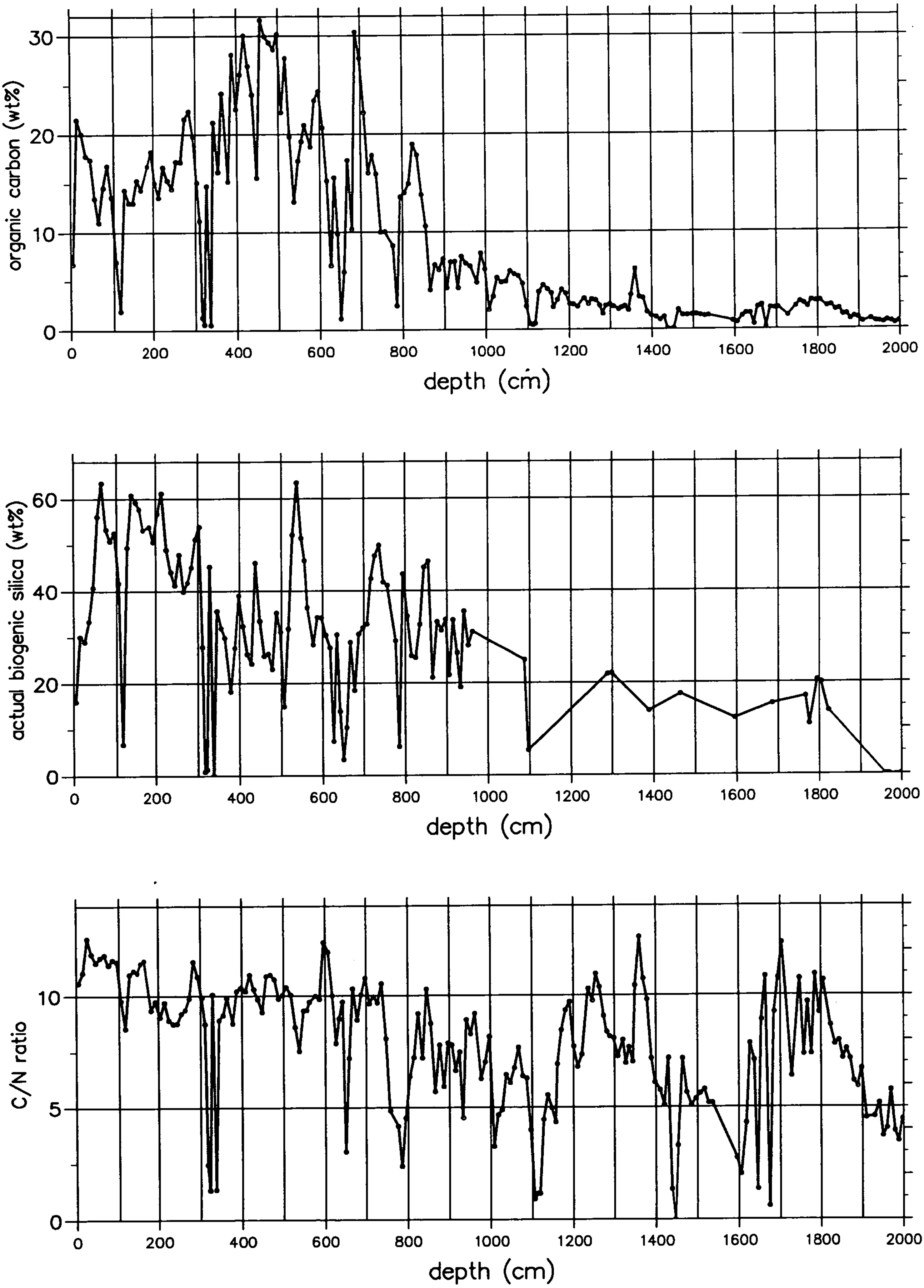


Fig. 4.11. Comparison of biogenic silica with organic carbon content and C/N ratio for upper 2000cm

coeval tephra layer at 785cm. This contrasts with the marked declines in organic carbon and C/N ratio between 810 and 750cm depth and supports the evidence from the C/N ratios that productivity within the lake may have declined to a much lesser extent than productivity of the surrounding higher vegetation at this time.

The Holocene is typified by biogenic silica contents between 30 and 63 wt%. During the early half of this period, biogenic silica is generally lower at around 30wt%, although peaks at 750cm and 540cm show brief periods of very high values. Above 350cm, however, values rise to a sustained high for the next 300cm and range from 40 to 60wt% SiO_2. In the most recent part of the Holocene, above 50cm depth, there appears to be a pronounced reversal and values decrease sharply towards the present.

Discussion

As with organic carbon, biogenic silica content is influenced by productivity, preservation and dilution.

1) PRODUCTIVITY As with the other components of the lake plankton, the productivity of diatoms is influenced mainly by epilimnion nutrient supply and usually to a lesser extent by temperature and light conditions. Increased availability of nutrients will in general favour increased productivity by plankton as a whole, but diatoms differ from other plankton in their requirement of silica as a key nutrient. Kilham (1971) recognised that when silica demand is high (e.g. due to increased diatom productivity) and available silica becomes depleted, diatoms are replaced by algae not requiring silica (i.e. green and blue-green algae). Tilman et. al. (1986) studied natural assemblages of lacustrine plankton under controlled laboratory conditions of varying nutrient ratios (Si/P, N/P), light and temperature levels. Due to ecological competition diatoms increased in dominance under conditions of high Si/P and N/P nutrient ratios and were the dominant planktonic group at a wide range of nutrient ratios when temperatures were below 14°C. On the other hand, at very low light levels (perhaps due to increased water turbidity) diatoms were replaced by green algae as the dominant group and at progressively higher water temperatures green followed by blue-green algae became dominant. At temperatures above 24°C blue-green algae dominated a wide range of nutrient ratios.

Sustained high diatom productivity therefore requires a sufficient supply of silica as well as phosphorus. Both these nutrients may be derived from external sources or from the internal nutrient load. It is found that phosphorus is normally recycled at a much faster rate than silica in the water column or lake sediment zone (Schelske et. al., 1986). Phosphorus release is tied up with the microbial breakdown of organic matter which is a faster process than the chemical or physically controlled dissolution of biogenic silica (in most environments). This means that a higher net amount of silica is lost to the sediments and so it is more necessary for this nutrient to be replaced by continued *external* supplies.

2) PRESERVATION According to Engstrom and Wright (1984) diatom frustules seem to be well preserved in the sediments of most lakes despite the potential for silica dissolution. Possible degradation can occur through mechanical break-up under conditions of high turbulence or through dissolution. The latter has been associated with particular environments including deep lakes with silica-undersaturated water columns, areas where sedimentation and burial are slow and high pH settings (e.g. in lakes where carbonates are being secreted). The diatoms may to some extent be protected from these effects by their organic coatings or by the presence of multivalent cations in the silica structure. It is believed that preservation changes are of secondary importance to productivity in interpreting the Monticchio record and that in general the level of diatom preservation is good (B. Zolitschka, pers. comm.). However, a systematic examination of the core by S.E.M. would be required to confirm this, and it is possible that the diatom component may have suffered from some dissolution in diatom-poor areas or where carbonate sediments are found.

3) DILUTION It is expected that biogenic silica content would be influenced by the same dilution effect from increased clastic input that causes organic carbon content to be reduced. In general, primary productivity is thought to be the main influence on the record of biogenic silica content and only in areas of high tephra or turbidite input is dilution considered the definite primary factor. However, during the Holocene period where clastic mineral matter is scarce, it is possible for mutual dilution effects to exist between the biogenic silica and organic carbon contents. It is not possible to evaluate whether silica input increased or organic carbon flux decreased without the availability of accumulation rate data.

Interpretation

The interpretation of biogenic silica content may be related to the models explaining organic carbon deposition which were presented in Figs. 4.4a. 4.4b.. According to the new model (Fig. 4.4b.), sedimentation during the earlier history of the lake (below 2000cm depth) took place under conditions of lower nutrient supply from the catchment. Therefore rates of phophorus supply were limited, although supply of silica through mature-stage soil weathering may not have been as reduced in relative terms. Under these conditions diatoms could outcompete other planktic groups and they therefore represent the dominant component of the biological material sedimented at that time. Only a relatively small increase in phosphorus supply might be required to cause a large increase in diatom productivity (Schelske et. al., 1986). This is what may have occurred during the proposed interglacial periods at 4900 and 3400cm when enhanced terrestrial vegetation cover favoured the leaching of slightly higher levels of nutrients (in particular P) from the catchment area. This is reflected in dramatic rises in biogenic silica content, although the response of organic carbon content (representing overall productivity) is more subdued.

During the later history of the lake (above 2000cm depth) the renewed nutrient supply from freshly leached volcanic material in the catchment could have caused an increase in the supply of phosphorus relative to silica, perhaps culminating during the maximal leaching conditions of the Holocene and latest-glacial periods. This would cause the dominance of diatom contributions to be reduced and is reflected by the more subdued trends in the biogenic silica profile when compared against organic carbon rises. It is possible that the lower than expected biogenic silica maximum in the zone between 1600 and 1800cm depth may be connected with lower rates of preservation. This area is characterised by significant carbonate precipitation and higher pH conditions at this time could have accelerated the rate of diatom dissolution (Newberry and Schelske, 1986).

During the Holocene the C/N ratio remains at a similar value throughout and so variations in biogenic silica and organic carbon content should mainly reflect patterns of relative dominance amongst the lower plants or phytoplankton of the lake. The early part of the Holocene (300 to 700cm) shows reduced dominance by diatoms and it is expected that green algae (and blue-green algae) reached their peak here. In contrast, the later Holocene sees a renewed dominance from diatoms until the uppermost 50cm of the record. These changes may reflect mainly nutrient availability, for example in terms of lower Si/P ratios during the earlier Holocene. It may also be possible that temperature has had an effect on the planktic populations. For example, the presumed increase in green algae during the early Holocene might partially be attributed to higher temperature levels (Tilman et. al., 1986). It is not certain how sensitive the changes in plankton dominance might be in this environment and so both nutrient and temperature changes remain reasonable possibilities. Nutrient changes would probably be related to external supply either through climate-vegetational induced changes in leaching inputs or modifications in nutrient supply associated with tephra deposition. It is possible that the decline in diatom dominance suggested above 50cm depth is connected with an increase in phosphorus loading from human activities in the catchment.

It would be very useful if the diatoms could be studied in their own right as more detailed information would be available from this work. As an indicator of total diatom abundances, biogenic silica has provided additional ideas on productivity and past nutrient conditions in Monticchio and may more sensitively reflect this information than the organic carbon profile in lower parts of the core.

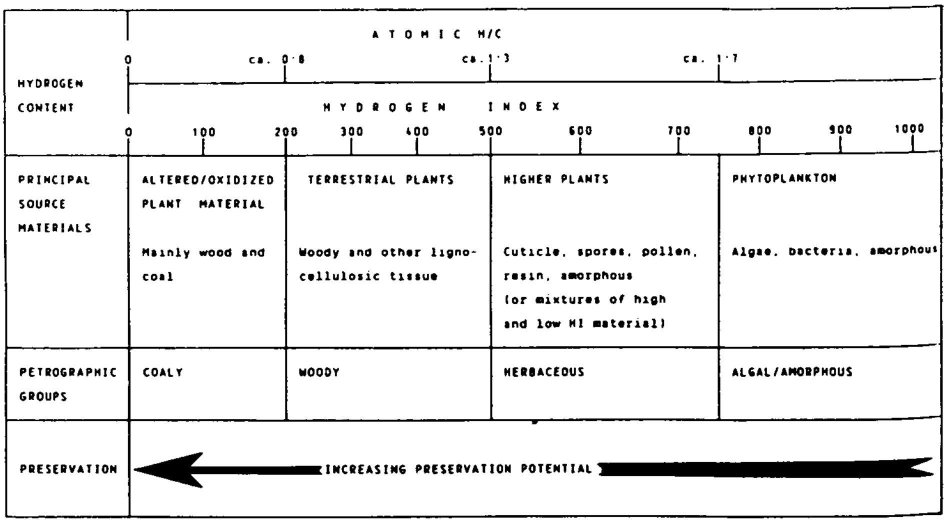
HYDROGEN INDEX

Hydrogen index (HI) values have mainly been applied in the study of petroleum source rocks and the kerogen characterisation of ancient sediments (Tissot and Welte, 1984). In the last decade the measurement has become used more frequently on younger lake sediments and Talbot and Livingstone (1989), in recognising its value, have recommended that pyrolysis techniques should become a standard part of palaeolimnological investigations.

Like C/N ratios, hydrogen index can give further information on the sources and diagenetic state of the sediment organic matter. It provides an indirect estimate of the atomic H/C ratios of the *kerogen* (i.e. the >90% of organic matter in the sediment that is not soluble in organic solvents) and is determined from the measurement of the hydrocarbon yield of the kerogen when it is subjected to thermal cracking. This has become a standard tool in organic geochemistry and petroleum geology due to its convenience over the direct elemental analysis of kerogen (Espitalié et. al., 1985).

Care must be taken when analysing sediments with low organic carbon contents due to possible mineral matrix effects (Peters, 1986). This may be a particular problem in organic-poor clays and carbonates where the matrix may retain a high proportion of the liquid hydrocarbons produced during pyrolysis. In the study of Lac du Bouchet (Bertrand et. al., 1992), it was thought that hydrogen index was a reliable indicator in sediments containing >0.5wt% organic carbon. The sediments from Lago Grande di Monticchio generally contain more than 1wt% carbon and are thought to be little affected by this phenomena.

Previous studies of lacustrine organic matter have emphasised to varying degrees the relative importance of source and diagenetic factors on hydrogen index. Fig. 4.12. shows typical HI values that have been associated with fresh and altered organic material. It can be seen that values over 750 should be related to the presence of a primarily planktonic matter source. However, more recent data has confirmed that many samples of amorphous or planktonic organic matter may possess HI values below 600 and that, when altered, this component can display values of 100-300, similar to woody material (R. Tyson, pers. comm.). It is possible for HI values below 500 to be interpreted in terms of one or more source components in a mixture and/or the presence of altered material. The progressive



	ATOMIC H/C: 0 — ca. 0·8 HYDROGEN INDEX: 0, 100, 200	ca. 1·3 300, 400, 500	ca. 1·7 600, 700	800, 900, 1000
HYDROGEN CONTENT				
PRINCIPAL SOURCE MATERIALS	ALTERED/OXIDIZED PLANT MATERIAL Mainly wood and coal	TERRESTRIAL PLANTS Woody and other ligno-cellulosic tissue	HIGHER PLANTS Cuticle, spores, pollen, resin, amorphous (or mixtures of high and low HI material)	PHYTOPLANKTON Algae, bacteria, amorphous
PETROGRAPHIC GROUPS	COALY	WOODY	HERBACEOUS	ALGAL/AMORPHOUS
PRESERVATION	INCREASING PRESERVATION POTENTIAL			

Fig. 4.12. Variations in Hydrogen Index for different organic matter groups (from Talbot and Livingstone, 1989)

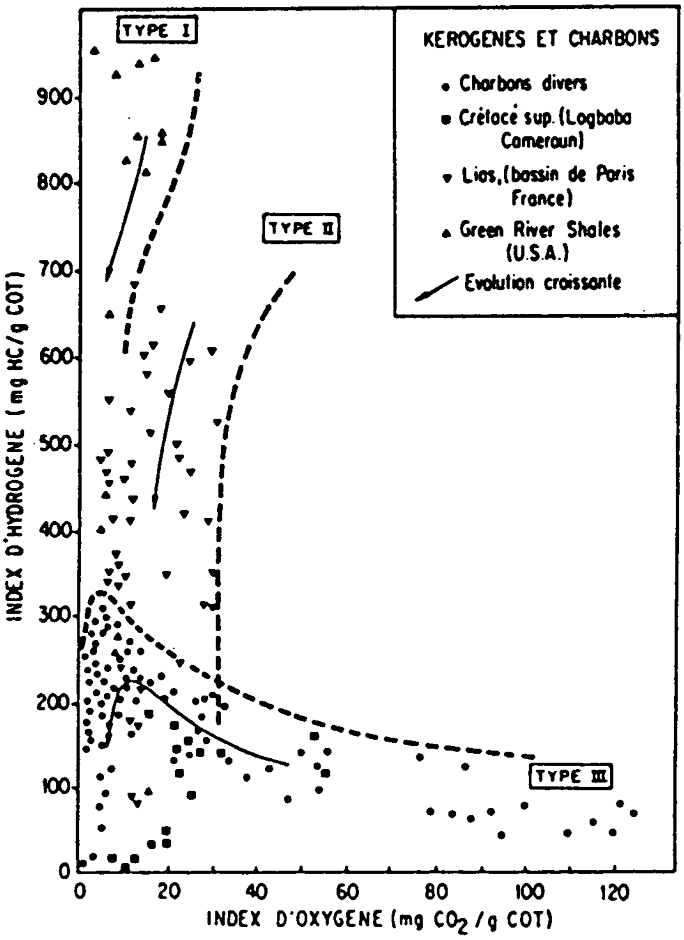
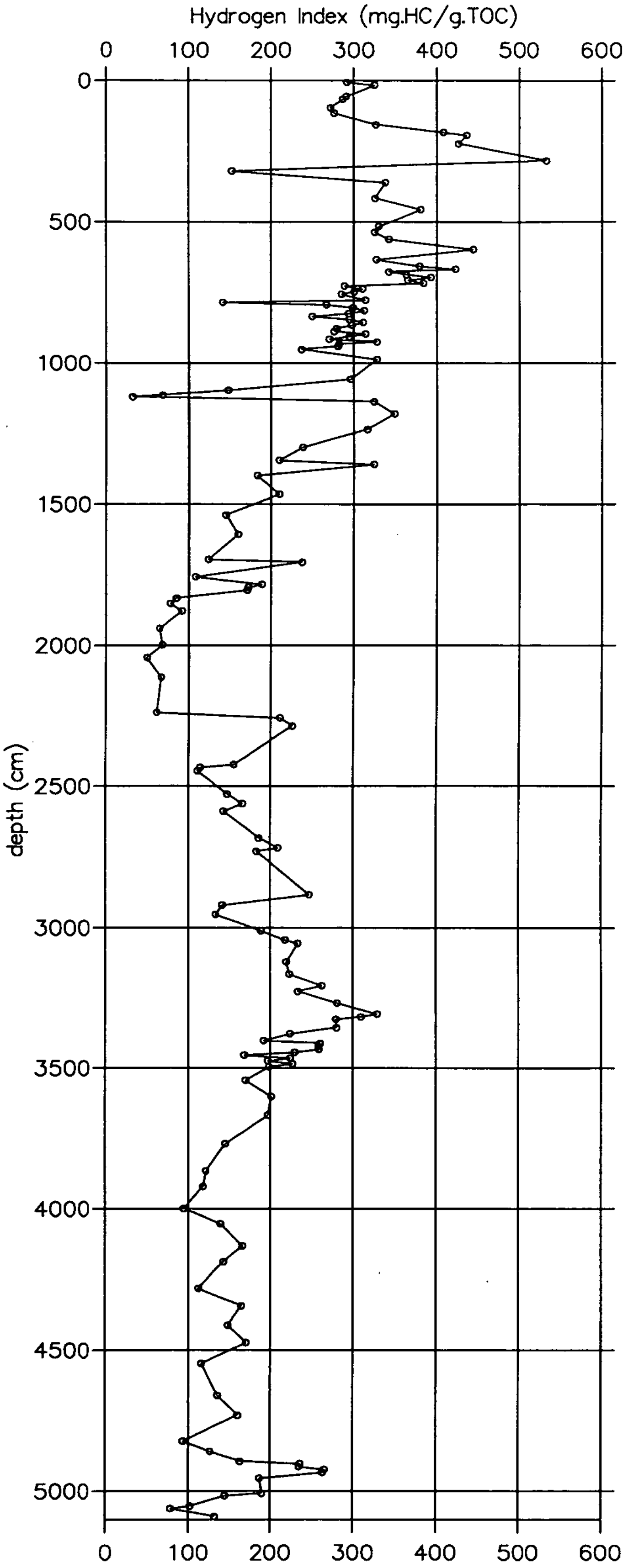


Fig. 4.13. Evolution of kerogen in terms of Hydrogen Index and Oxygen index values with progressive burial (Espitalié et. al., 1985)

reduction in hydrogen index associated with kerogen maturation (under oxygen deficient conditions) is illustrated in Fig. 4.13. which shows how the main classes of kerogen evolve with burial. Type I kerogen which equates with planktonic lacustrine organic matter has initial HI values greater than 800, but these fall as burial and thermal evolution take place (Tissot et. al., 1974). The arrows suggest that eventually this material may evolve into a polyaromatic carbon-rich residue containing virtually no hydrogen. These changes are in the context of much longer time spans than the present study and Tissot and Welte (1984) consider that young sediments should retain much of the variation inherited from their organic sources.

In her study on Lac du Bouchet, Truze (1990) interpreted the hydrogen index results in terms of sediment source mixtures. Two principal organic sources were proposed: a high HI planktonic component and a low HI detrital component. These were modelled with mixing equations to represent the sediment composition. The Holocene period (a lacustrine planktonic episode) might have been expected to display HI values of over 700. The modest values of 400-500 that were found were interpreted as the result of some "detrital" organic matter also being present. It was thought that diagenesis provided a limited influence on the record since a simple time-dependent evolution path did not exist in the HI profile. However, in a later study (Bertrand et. al., 1992) the influence of 'amorphous-degraded' matter in creating lower HI values was given greater emphasis for this site.

Talbot and Livingstone (1989) interpreted hydrogen indices in mainly diagenetic terms for their reconstruction of lowered lake levels from two African sites. They associated HI decline with the selective removal of labile compounds by bacterial respiration and inorganic oxidation during periods of emergence or bottom water oxygenation. At these times the sediment record contained low levels of inert organic matter having considerably lower values (HI<100) than the surrounding sediments (HI>400). Hollander et. al. (1992) also associated changes in hydrogen index with degree of preservation of the organic-rich sediments in a Swiss lake. Parallel work had shown that not only did the relative proportions of terrestrial versus aquatic matter sources remain constant during the period under study, but that there was no change in dominance between the phytoplankton groups present in the aquatic matter either. The independent process of early diagenesis was ruled out, but it was thought that changes in HI reflected changes in surface water productivity and its subsequent influence on oxygen depletion causing change in the quality (and quantity) of the organic matter preserved.



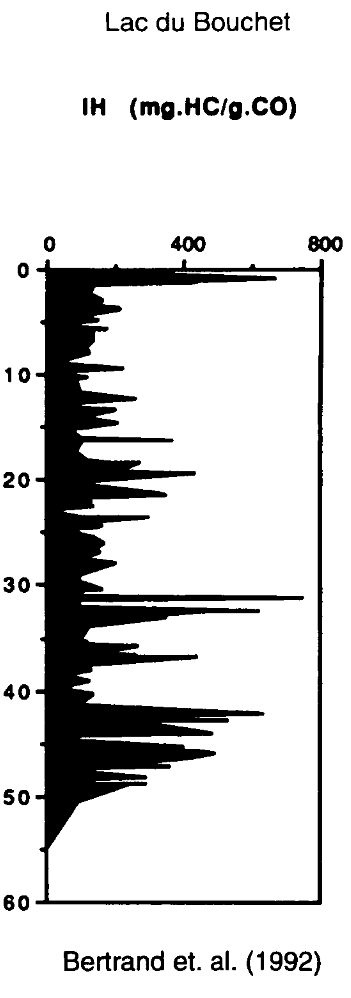


Fig. 4.14. Comparison of Hydrogen Index values for Monticchio and Lac du Bouchet

These studies illustrate that hydrogen index may be controlled by either organic matter source *or* alteration depending on the environment. The possibility also exists that both factors may dominate at different times in the same setting or record.

If the Monticchio record is examined (Fig. 4.14.) the HI profile appears to show similarites with both the organic carbon and biogenic silica profiles previously presented, but is more at variance with the C/N ratio profile. The highest values for hydrogen index lie in the Holocene period and range from 300 to 500. A peak occurs at 250cm during a time when biogenic silica content is also maximal. After a 'plateau' phase between 750 and 1200cm values drop to a minimum in the clastic-dominated zone at 2000cm depth. The lower interglacial (or interstadial) horizons identified at 3400cm and 4900cm depth also show relative HI maxima, although values here never rise above 300. HI values for most of the core profile below 2000cm lie in the 100 to 200 range typical of major contributions from altered/oxidised organic material and/or woody or higher plant tissue (Fig. 4.12.).

A hydrogen index profile from Lac du Bouchet is also shown in Fig. 4.14. for comparison. Like Monticchio this profile shows a considerable correlation with organic carbon content (c.f. Fig. 4.3.). Higher HI values up to 750 occur in the Bouchet record for brief periods, but most points lie between 100 and 500 as in Monticchio.

From the C/N ratios in the upper part of the Monticchio record it was suggested that the organic matter in the Holocene sediments contains a major planktonic component with some contribution from terrestrial organic sources. A major planktonic component *might* be expected to give HI values above 500 and it is not certain whether the modest HI values of 300 to 500 represent a simple mixture (terrestrial and planktonic) of unaltered sources or a dominant component of low HI (partially degraded?) planktonic matter. It is possible that both oxidative and anaerobic forms of alteration may have affected the planktonic material during early diagenesis. Perhaps also a quantity of reworked organic matter is present. This could be linked with reasons for the excessively old bulk radiocarbon dates described in Chap. 3.

The plateau seen during the glacial-Holocene transition between 750 and 1250cm depth is in concordance with the biogenic silica record and suggests that a major part of the lacustrine productivity maintained itself at moderately high levels during this period of change, and was not adversely affected by a possible Younger Dryas event, if present. From 1250 to 2000cm depth the decline in HI paralleled by declines in organic carbon and biogenic silica content suggest a marked decline in organic productivity. The HI values below 200 that are encountered in this area could reflect the presence of mainly altered organic matter (probably due to increased oxygenation and microbrial breakdown) with possible additions of old reworked organic matter from the catchment.

It is thought that the generally low HI values from 2000cm downwards are reflective of changes in the degree of organic matter preservation coupled with productivity. If primary source factors were the only influence, it would be difficult to reconcile the HI values with the C/N profile. In particular, the lower C/N ratios seen in glacial areas (suggesting dominance of plankton) would be expected to correspond with increased HI values, which is not the case. This can be explained if the glacial areas contain low amounts of highly degraded planktonic matter (i.e. of low HI value) and contain a significant quantity of humic- or lignin-bound nitrogen. In contrast the interglacial (interstadial) areas will contain higher quantities of both planktonic and terrestrial organic matter which has perhaps been deposited under more oxygen depleted conditions. This will give somewhat higher HI values and with the reduced process of nitrogen incorporation during humification and/or the increased relative contribution of higher plant matter will lead to higher C/N ratios.

In conclusion it is thought that primary productivity and organic sources exert a major influence on the sedimentation record, but that lower productivity may be connected with lower preservation through the increased availability of oxygen during diagenesis and the slower rates of organic matter deposition-burial. These changes are ultimately governed by the influence of nutrient supply and its control on production. Evidence from radiocarbon dating to suggest the importance of redeposited older organic matter is offered some support by the hydrogen index values.

BROMINE and IODINE

The profile for bromine (Fig. 4.15.) is highly correlated with that for organic carbon, particularly over the upper 1500cm of the sequence (r=0.938). Outside the Holocene part of the profile where concentrations can exceed 100ppm, the concentration of bromine tends to lie below the 20ppm level which is normal for freshwater lacustrine sediments (Fuge, 1978a). It is known that sediments can be enriched in Br due to the presence of plant material (Cosgrove, 1970) and that the element is concentrated in humic layers of soils (Vinogradov, 1959). Thus the unusually high bromine values up to 120ppm are thought to be a consequence of the unusually high organic matter contents of the Holocene section.

It is possible that the element may be largely derived from weathering of the catchment rocks which contain 5-10ppm Br (Table 2.1.) On the other hand, the lake sediments have more

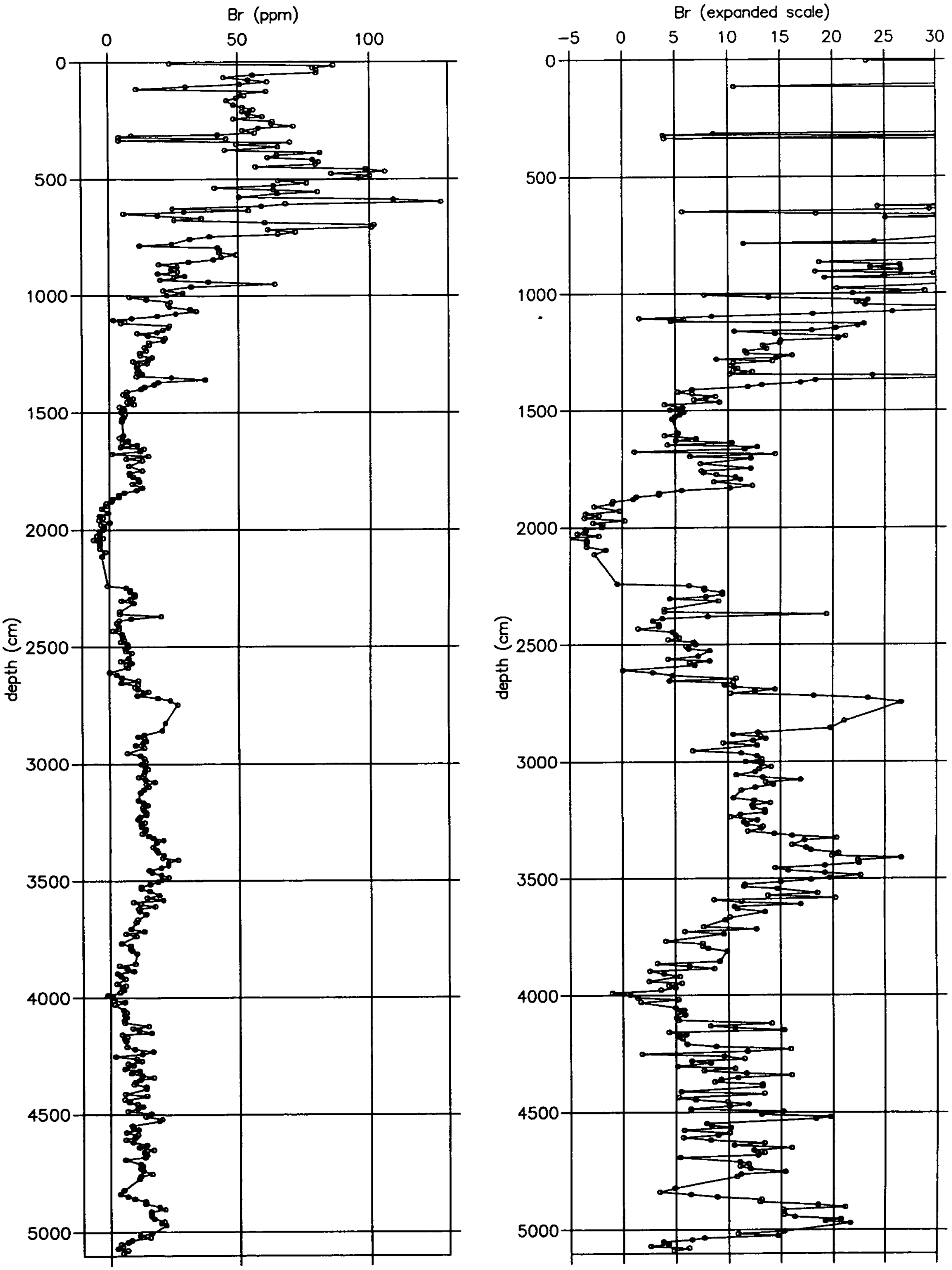


Fig. 4.15. Bromine content

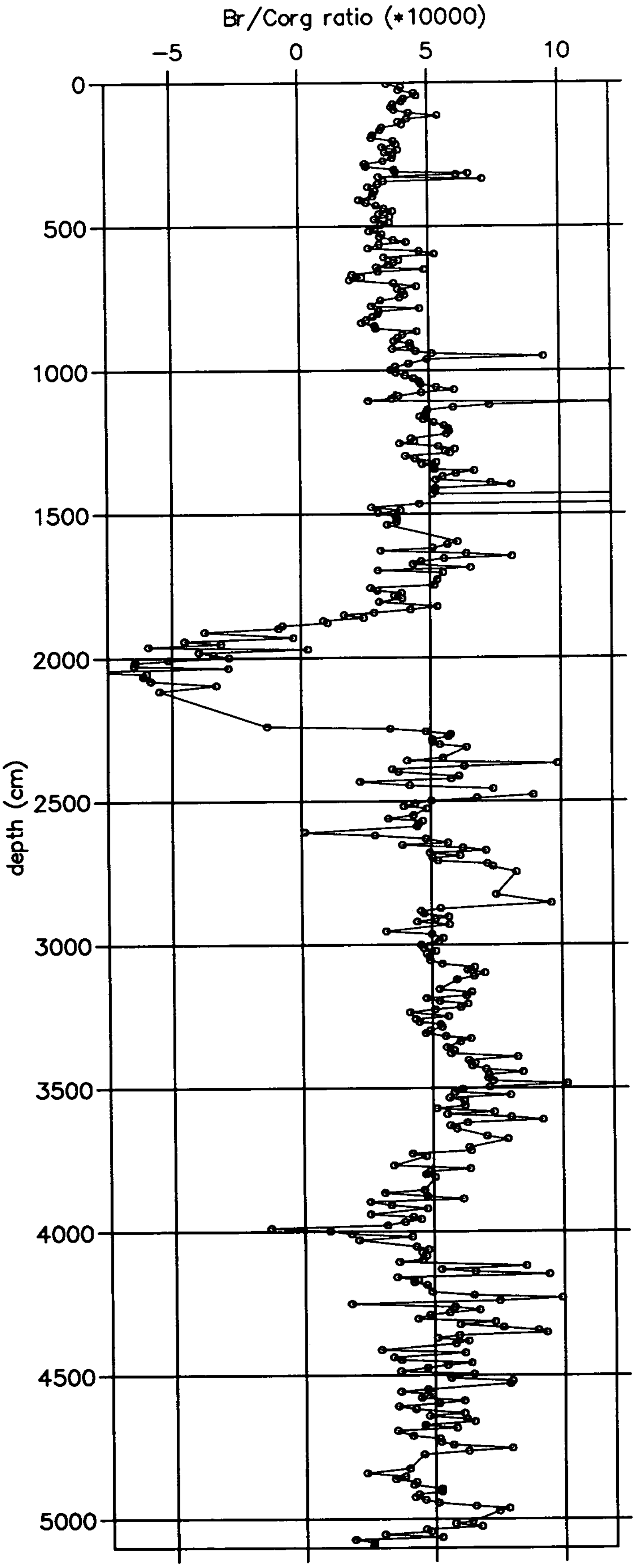


Fig. 4.16. Bromine/organic carbon (Br/C_{ORG}) ratio

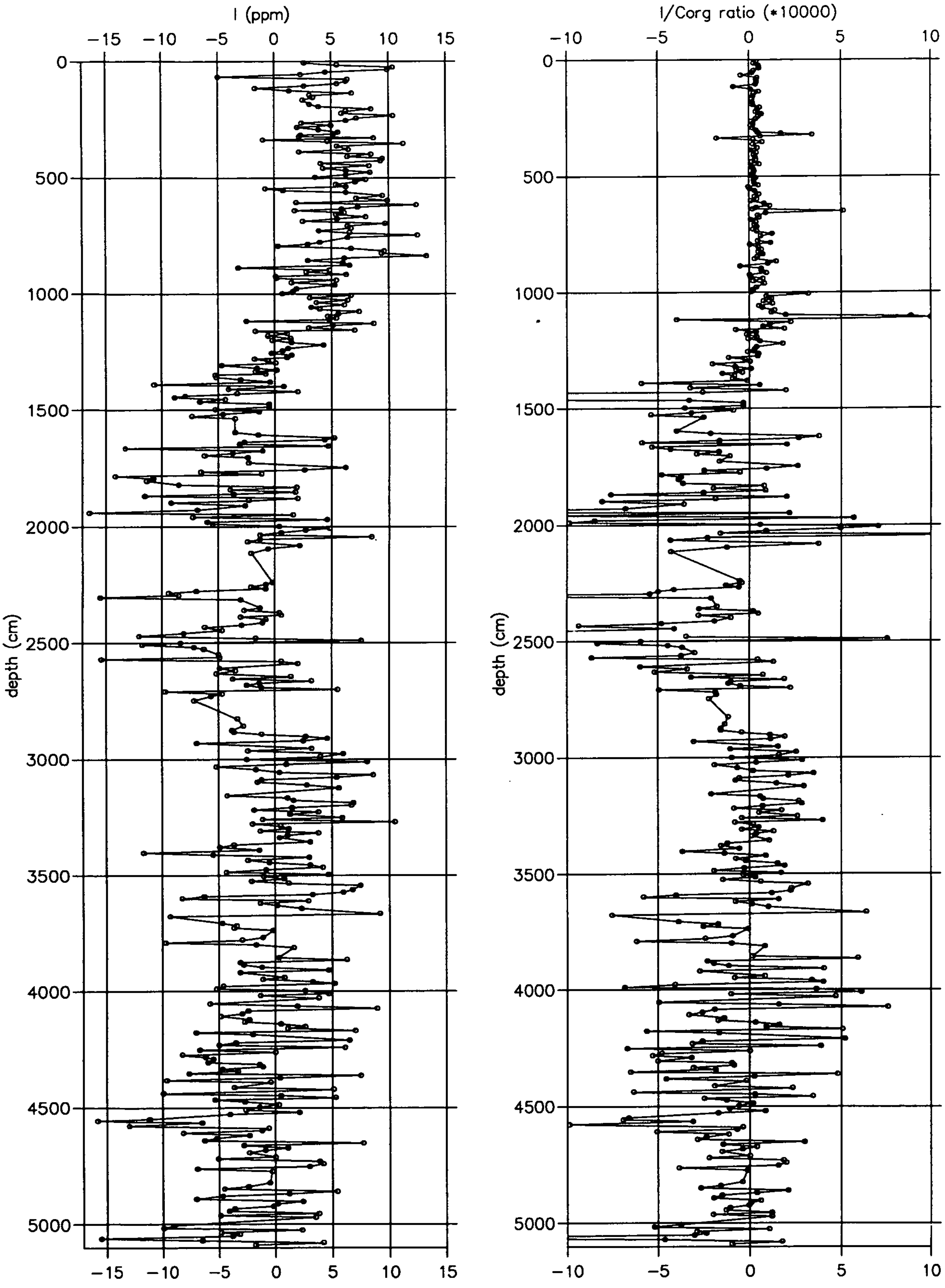


Fig. 4.17. Iodine content and I/C_{ORG} ratio

enriched compositions and a major supply of the halogens is thought to occur through the atmospheric transport of ocean-derived aerosols (Mackereth, 1965). Changes in Br/organic carbon ratios might therefore reflect the climatic 'oceanicity' (wind conditions, air temperature, etc.). Mackereth (1965) found independent variation between halogen and organic carbon contents in the post-glacial period from certain lake sediment records and was able to divide the post-glacial into three stages of differing 'oceanicity of climate'. However, he recognised that in addition to climatically controlled supply changes, the halogen content could also be influenced by changes in the chemistry and ionic balance of catchment soils. In addition the selective effects of diagenesis and change in the type of organic matter sources cannot be disregarded. Examination of Br/C_{ORG} ratios from the Monticchio core (Fig. 4.16.) shows that marginally higher ratios occur between 850cm and 1450cm than in the Holocene zone above. Thus, if the ratio depended *only* on rate of halogen supply from rainfall, the ocean (Mediterranean Sea/N Atlantic?) may have had more influence on local climate during this earlier period. However the ratio is more or less constant at around $5x10^{-4}$ for much of the profile and it is difficult to make sound interpretations of any trends seen. Positive spikes associated with some of the tephra samples show that these layers have relatively high (mineral-associated) bromine contents in comparison to their low organic carbon values, while the area of negative ratios around 2000cm depth is caused by erroneous XRF concentration data.

The iodine profile (Fig. 4.17.) is particulary noisy and the errors bars associated with the XRF determination are of similar magnitude to the trends exhibited (Appenidx 1). Selective examination by wet chemistry (see Appendix 1) suggests that the XRF measurements are of the right order of magnitude and that the Monticchio sediments do not contain iodine concentrations above 10ppm. Values below 10ppm appear normal for freshwater lake sediments (Fuge, 1978b) although values up to 35ppm have been documented, particularly from seaward localities (Pennington and Lishman, 1971). Supply from weathering of the catchment rocks is thought to be minimal as these contain virtually no iodine (Table 2.1.) and so supply by atmospheric processes is assumed to be dominant. In spite of the values measured being close to the XRF detection level, it would appear that the sediments above 1100cm depth show somewhat higher iodine concentrations than those below. Like bromine, iodine is known to be associated with organic matter content in both marine (Price et. al., 1970) and lacustrine sediments (Pennington and Lishman, 1971) and so a simple relationship with the elevated organic matter content of this zone can be inferred. A minimum zone appears to exist around 2000 to 2500cm depth, but the amount of noise makes the identification of real trends difficult.

Attempts have been made to use the iodine/organic carbon ratio to infer past rainfall changes or soil development (Pennington and Lishman, 1971) and in the marine environment to recognise past oxygenation conditions in the surface sediment zone (Pedersen et. al., 1988). The I/C_{ORG} profile from Monticchio (Fig. 4.17.) shows no convincing trends and values tend to remain below $1x10^{-4}$ throughout. Due to the difficulty in obtaining a reliable iodine profile with the techniques used it is not thought possible that such information can be extracted from the data and the relationships will not be discussed further.

CARBON STABLE ISOTOPE RATIO ($^{13}C/^{12}C$)

Interest in the stable carbon isotopic ratio of organic matter (Rounick and Winterbourn, 1986) is centred on its possible relations to climatic change. This response to climatic change may be manifest through wide-reaching phenomena (e.g. change in temperature, change in the atmospheric CO_2 reservoir) or more local and indirect effects (e.g. change in the types of organic matter being sedimented in response to climate). It would be particularly interesting if trends of regional or global significance could be identified (Jasper and Gagosian, 1989), but it is possible that local factors dominate or at least confuse signals which might be more widely correlated.

Lacustrine studies have found both negative (Håkansson, 1985) and positive (Nakai, 1972) shifts in $\delta^{13}C$ associated with the change from glacial to interglacial conditions, and some studies (Harkness and Walker, 1991) find $\delta^{13}C$ peaks occurring **between** these two climatic extremes within the zone of transition. In interpreting the isotopic record from Monticchio, use will be made of the other biological parameters so far measured. However, none of these is found to show a simple coherent relationship with $\delta^{13}C$.

The stable carbon isotopic ratio measured on bulk organic matter is shown in Fig. 4.18. The $\delta^{13}C$ values are presented relative to the PDB standard and the C/N ratio profile is shown for comparison. Isotope values determined on the Monticchio core vary between -27 and -21‰. This could be said to typify a fairly average mix of lacustrine organic matter (Deines, 1980). The two most striking features of the profile are the shift from -22.1 to -25.3‰ seen between 950 and 750cm depth (i.e. during the late-glacial transition) and the pronounced minima in values at around 3300cm depth which may correlate with the Eemian interglacial. This latter zone is preceded by an even bigger negative shift of 5‰ between 3500 and 3350cm. Both features are shown enlarged in Fig. 4.19.

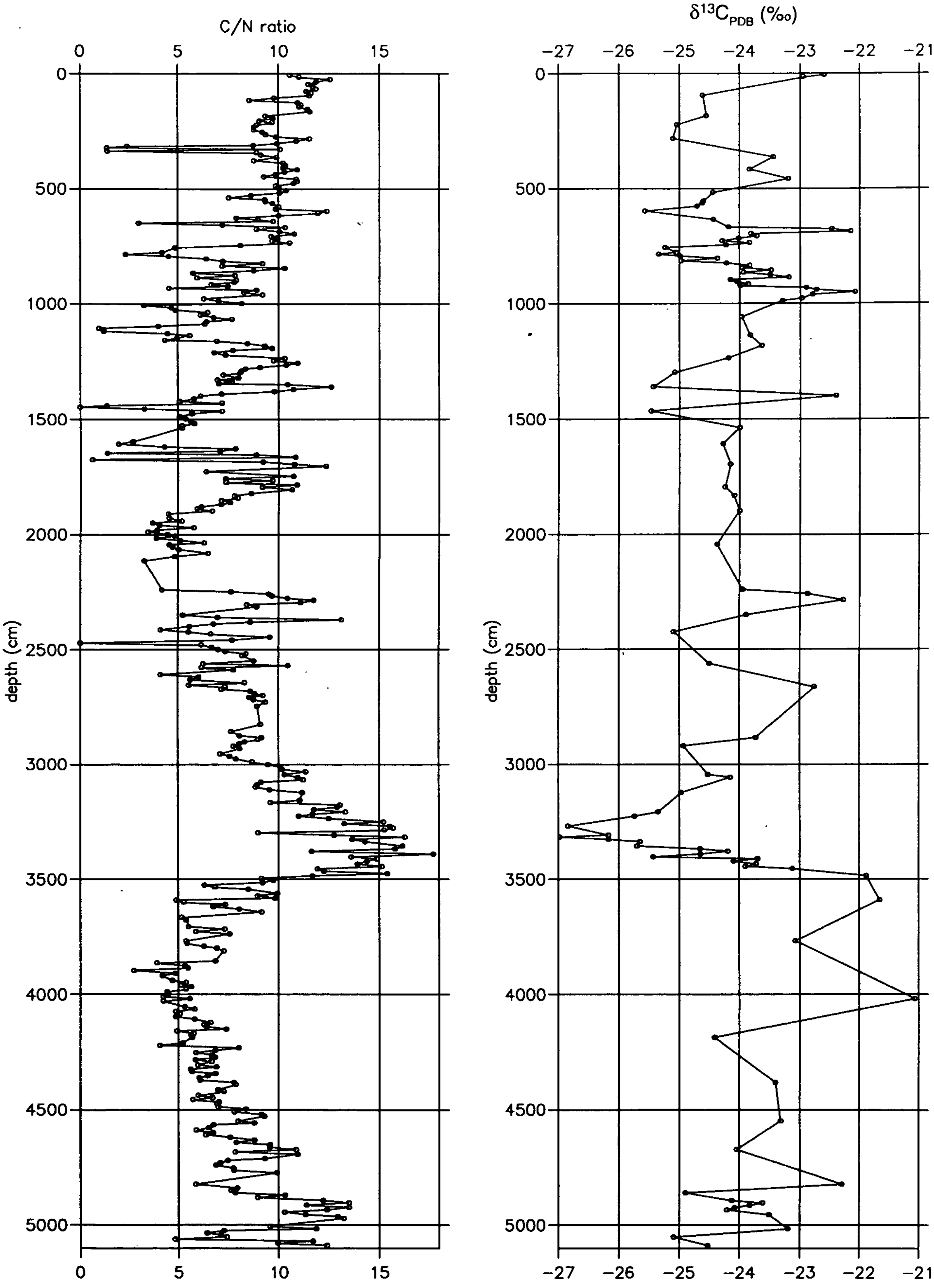


Fig. 4.18. Stable carbon isotopic ratio of bulk organic matter and C/N ratio

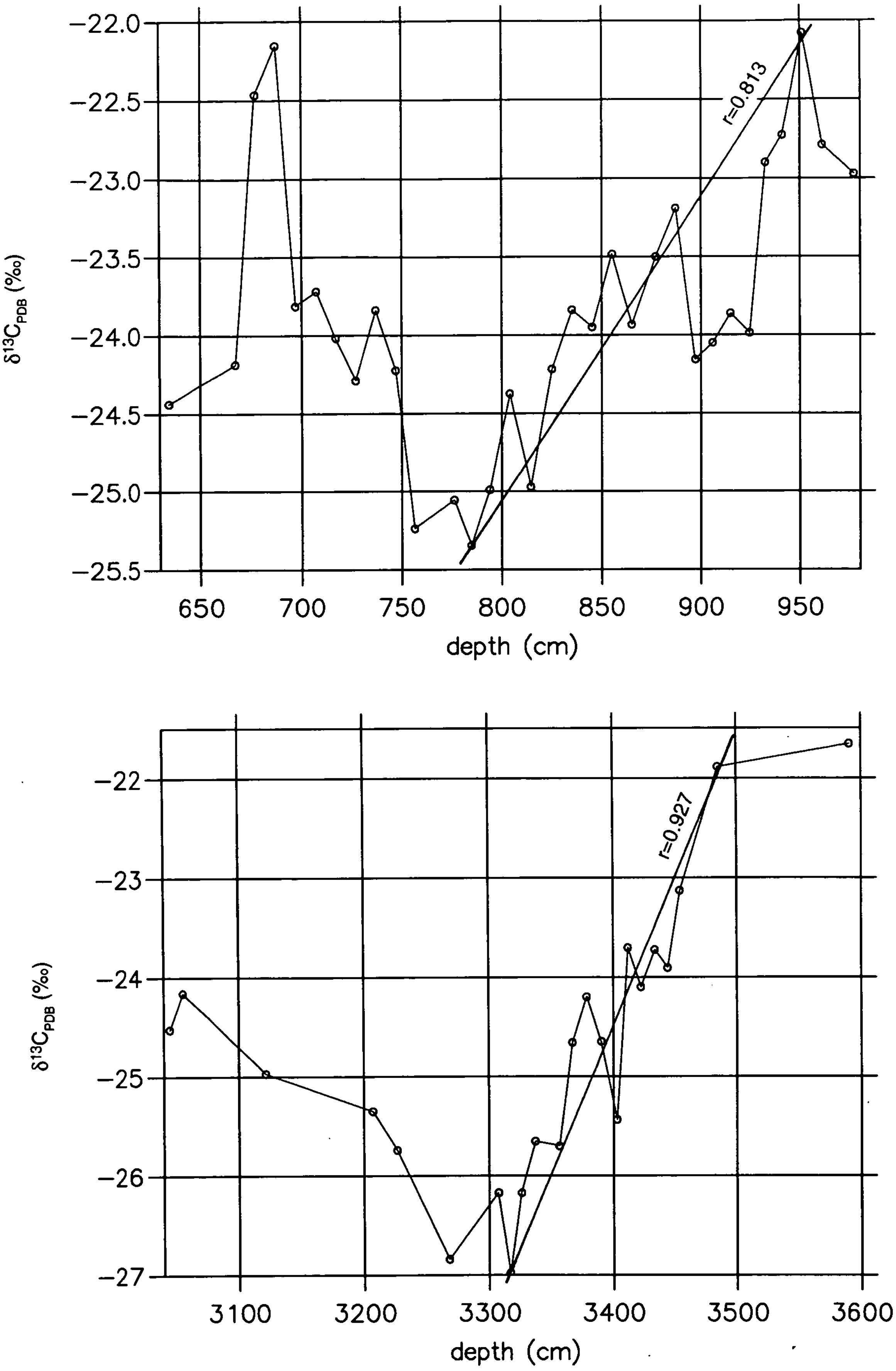


Fig. 4.19. Examination of zones containing pronounced $\delta^{13}C$ shifts

Outside these two 'zones of interest' values fluctuate around an average value of -24‰. Between 3500 and 4800cm the $\delta^{13}C$ values are typically higher than this average in what is thought to be a glacial period. The interglacial (or interstadial) at 4900cm depth differs from that at 3300 to 3400cm in not showing a pronounced minimum. Instead, values vary between -25 and -23‰. The glacial period from above 3000cm to around 1000cm depth shows fluctuations between -25 and -22‰, but most values lie close to the profile average of -24‰. Following the pronounced negative shift at the end of the last glacial period the Holocene begins with an abrupt shift back towards isotopically heavier carbon between 700 and 675cm. Above this values fall to a minimum of -25.6‰ at 600cm and then rise to a second maximum between 500 and 350cm depth. The upper part of the Holocene contains a further zone of low $\delta^{13}C$ values between 300 and 100cm depth before an increasing trend towards higher values as the top of the core is reached.

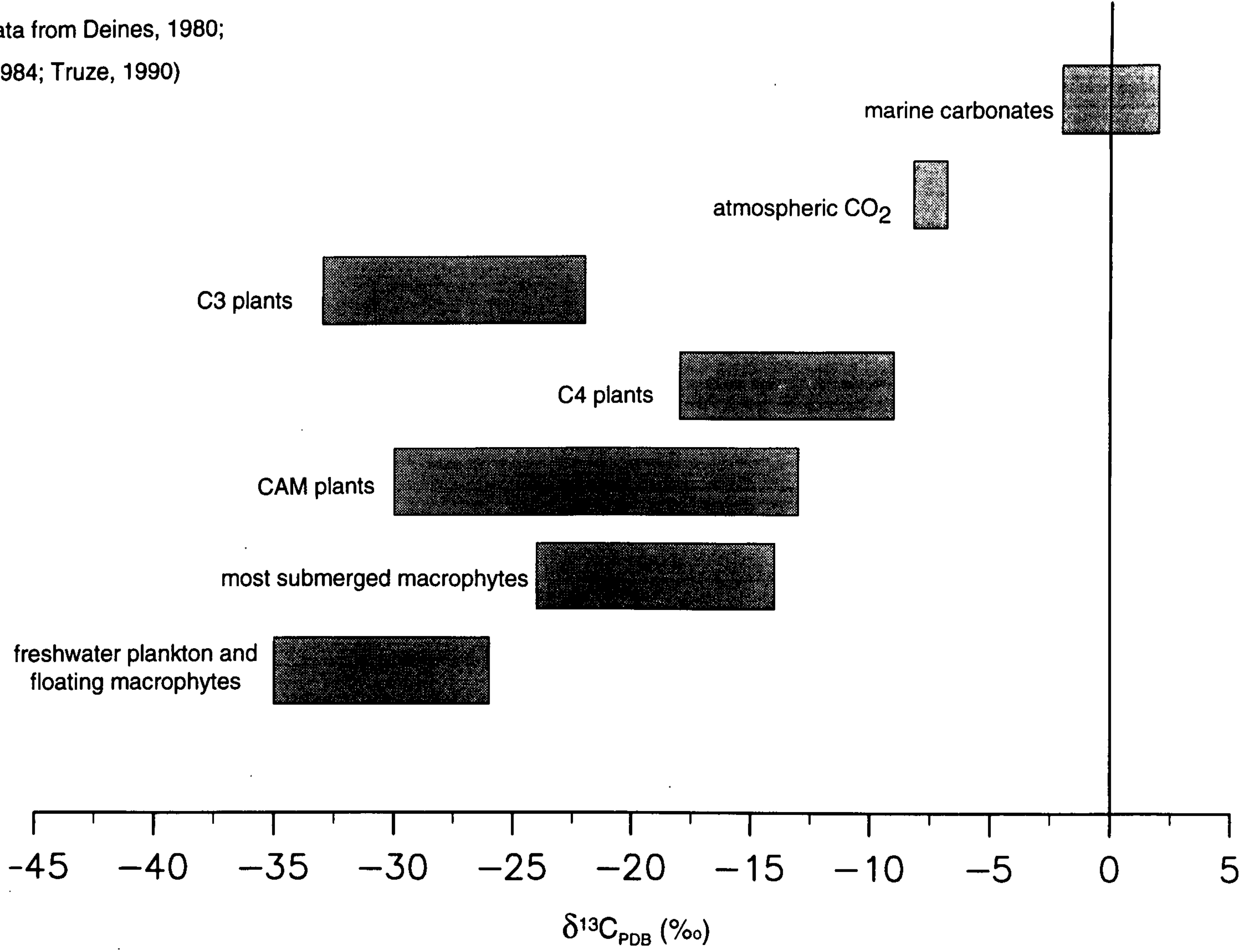
Discussion

The factors thought to cause changes in the $^{13}C/^{12}C$ ratio of sedimentary organic matter are reviewed by Stuiver (1975), Deines (1981) and Håkansson (1985). In this discussion they are divided into organic matter source changes, diagenetic fractionation effects and changes in the atmospheric carbon reservoir coupled with temperature changes.

SOURCE FACTORS Photosynthetic fixation of carbon into living organisms involves relatively large isotopic fractionations (often up to 20‰) with respect to the inorganic source reservoir. The degree that ^{12}C is preferentially incorporated into the plant tissue varies amongst different groups and species depending on the photosynthetic mechanisms employed (O'Leary, 1981; O'Leary, 1988) and the isotopic composition of the source reservoir. It is found that plants can be grouped into a number of major types which are characterised by particular ranges of $\delta^{13}C$ (Fig. 4.20.).

The majority of terrestrial vegetation belongs to the C3 group and typically has $\delta^{13}C$ between -23 and -33‰. It is thought that C3 plants dominate the terrestrial environment at Monticchio and therefore that the contributions from terrestrial organic matter at this site will most probably have values in the range shown. The C4 plant group consists of tropical grasses and plants associated with water-stressed environments and is characterised by heavier isotopic compositions between -8 and -19‰. It is possible that a small proportion of the grasses that grow at Monticchio belong to this group (B. Huntley, pers. comm.), but their contribution is not considered a significant influence during the Holocene. During the glacial periods when a steppe vegetation may have persisted the possibility of greater numbers of C4 plants cannot be ruled out altogether. A third group, the CAM plants, show a broad range

Fig. 4.20. Typical $\delta^{13}C$ ranges for major types of organic matter (based on data from Deines, 1980; Nakai, 1984; Truze, 1990)



of isotopic values, but these plants are succulents thought to be confined to truly arid regions.

Aquatic vegetation can be divided into plankton, floating macrophytes and submerged macrophytes. Most of these groups follow the C3 photosynthetic pathway, but $\delta^{13}C$ values can range more widely depending on the inorganic carbon reservoir utilised (Osmond et. al., 1981). In general, plankton and floating macrophytes photosynthesise from the atmospheric CO_2 reservoir and are characterised by relatively low $\delta^{13}C$ values which range between -26 and -34‰ (Nakai, 1984). In contrast, submerged macrophytes photosynthesise from a dissolved inorganic carbon reservoir which may be isotopically heavy (<+1‰) or light (>-21‰), and this can allow plant values to range from -10 to -50‰ (Osmond et. al., 1981). In many circumstances, however, the organic carbon of submerged macrophytes is thought to have a stable isotopic composition distinctly heavier than that of terrestrial C3 plants (LaZerte and Szalados, 1982). This is attributed to the greater diffusional resistance to CO_2 under water (reducing the effectiveness of kinetic fractionation) and the often higher $\delta^{13}C$ of dissolved inorganic carbon in comparison with atmospheric CO_2. From the review by Håkansson (1985), it would appear that values between -14 and -24‰ are most typical for submerged macrophytes and this will be taken as a reasonable range in the case of Monticchio.

It is possible that an increased rate of photosynthesis (driven by nutrient availability) could decrease the effectiveness of kinetic fractionation and lead to heavier isotopic compositions in the source planktonic matter deposited. A relationship between high $\delta^{13}C$ and organic productivity (organic carbon content) was found for Lake Biwa (Nakai, 1972), although the mechanism here may have involved change in the supply of CO_2 also.

DIAGENESIS It is possible that positive *or* negative shifts in $\delta^{13}C$ can occur during the diagenesis of sedimentary organic matter (Anderson and Arthur, 1983). The main chemical component groups in organic matter have been shown to vary with respect to the average $\delta^{13}C$ value of an organism (Galimov, 1981). Lignin and lipids which are particularly resistant to degradation tend to have lower $\delta^{13}C$ values than associated components such as cellulose or proteins. Benner (1987) found a marked decrease in sediment $\delta^{13}C$ with depth in a saltmarsh environment which was attributed to the progressive loss of other constituents relative to lignin. On the other hand, it is known that during organic decomposition bacteria preferentially utilise ^{12}C-enriched functional groups (Anderson and Arthur, 1983). This would tend to cause higher $\delta^{13}C$ values in the remaining organic matter. It is possible that both these effects may be compensated for by the incorporation of the bacterial decomposers (which have previously consumed the isotopically light or heavy carbon) into the sediment.

Methanogenesis is another diagenetic process which could potentially cause large isotopic shifts (Håkansson, 1985). Organic matter with very high $\delta^{13}C$ values might be produced through photosynthesis from the heavy CO_2 fermentation product, providing the CH_4 product was able to escape to the atmosphere. Alternatively, very low $\delta^{13}C$ organic matter could be photosynthesised from CH_4 which had been bacterially oxidised to CO_2. In many cases it is probable that the isotopically light CH_4 is oxidised before leaving the system and that this cancels out the effects of the isotopically heavy CO_2 byproduct.

Under certain conditions it is possible for an imbalance to allow major isotopic shifts due to diagenesis, but in most lake sediment reconstructions the major isotopic features have been attributed to source factors (Meyers, 1988; Talbot and Johannessen, 1992). As with the organic carbon and biogenic silica records it is thought that the major shifts and abrupt changes seen in the Monticchio $\delta^{13}C$ record are driven by primary source contributions. Smaller secondary effects from diagenesis may be connected with these changes in primary input.

ATMOSPHERIC CO_2 RESERVOIR and TEMPERATURE Evidence from the ice core record (Barnola et. al., 1987) has shown that atmospheric carbon dioxide concentrations were around 200ppmv during the last glacial period compared to 280ppmv in the Holocene. Further evidence for lower CO_2 during the glacial period has been found in marine (Jasper and Hayes, 1990) and lacustrine (Lal and Revelle, 1984) records. The latter authors used increases in the $^{14}C/^{12}C$ ratio of the sediments to infer lower atmospheric contents of carbon dioxide and included several major assumptions in their argument. Nevertheless, evidence appears to be widespread and possible mechanisms have been advanced to explain the change (Shackleton et. al., 1983). Most of the models that have been suggested involve increases in the amount of carbon dioxide absorbed in the ocean surface layers and/or the quantity of carbon stored within the marine sediment system.

It is not certain whether a lake system such as Monticchio would have responded sensitively to such changes. It would seem most appropriate to look for changes in the terrestrial organic component. This directly interacts with the atmospheric CO_2 reservoir whereas it is possible that organic components within the lake might be buffered by chemical changes in the dissolved inorganic carbon pool. A previous compilation of isotopic data from radiocarbon dated terrestrial material found that $\delta^{13}C$ values for glacial samples were on average 1‰ higher than values for the Holocene (Leavitt and Danzer, 1991). It was suggested that this might be caused by the less selective removal of ^{12}C by plants in response to the reduced CO_2 availability. An earlier study by Crayton and Epstein (1977) found that glacial wood samples were around 1‰ higher than more recent samples, but did not consider the differences statistically significant and so offered no interpretation of the trend. It would seem possible that some components of the organic matter at Monticchio could in theory record such a change, but it may be difficult identifying this from the mixture of organic material in the sediments.

In an opposing sense to the above trends (connected with reduced pCO_2), certain studies have shown evidence for glacial atmospheric CO_2 to be lighter in isotopic compositon than that of the Holocene. For example, a study of plant remains from packrat middens in North America (Marino et. al., 1992) suggested that glacial CO_2 may have been around 1‰ lower in $\delta^{13}C$. These isotopically lighter glacial ratios were suggested as resulting from lowered global levels of terrestrial biomass and reduced productivity in cold surface water zones of the ocean releasing more ^{12}C into the ocean-atmosphere system.

Temperature has been shown to influence the isotopic equilibrium between CO_2 and HCO_3^- in ocean water, causing slightly lower $\delta^{13}C$ dissolved CO_2 at lower temperatures (Deuser et. al., 1968). This could potentially cause planktonic organisms assimilating CO_2 in colder waters to be of a lighter isotopic composition. The effect is only around 0.1‰ per °C change in temperature and this would probably be outweighed by the much larger local variations resulting from source mixing and chemical changes seen in a lake. However, the effects of temperature may at the same time alter the amount of dissolved CO_2 available and this could enlarge the trend of decreasing $\delta^{13}C$ with decreasing temperature. It is not certain whether the temperature changes experienced at Lago Grande di Monticchio would provide a significant influence on the sedimentary $\delta^{13}C$ record through these mechanisms.

Past studies

Most lake sediment studies have associated $\delta^{13}C$ changes with lake and catchment flora changes, such as C3 versus C4 plant or terrestrial versus aquatic plant dominance, in resonse to changing climatic condtions (Talbot and Livingstone, 1984; Krishnamurthy et. al, 1986). Studies from European maar lake records have not been able to pinpoint exclusively the causes for change. In Meerfeldermaar changing contributions from C4 plants *or* an isotopically heavy indigenous algal bloom versus terrestrial C3 plant inputs is suggested, together with an unexplained 'regional or global shift' to lighter isotopic values during the glacial-Holocene transition (Brown, 1991). Also, smaller scale cycles observed in the Holocene section are related to changes in terrestrial vegetation dominance, but no evidence from pollen records etc. has been able to substantiate this. In Lac du Bouchet, Truze (1990) broadly associates lower $\delta^{13}C$ with interglacials and higher $\delta^{13}C$ with glacial periods, although this association does not entirely fit. Truze suggests that three factors may influence $\delta^{13}C$ in the record: 1) temperature, 2) mixtures of aquatic versus terrestrial sources and 3) the pCO_2 of the lake waters. These three factors are used to model the isotope record observed, but the individual magnitude and significance of their effects could not be properly tested.

In summary, the interpretation of the $\delta^{13}C$ record in lake sediments is complicated and the lakes that have been studied vary in their sensitvity to climatic change (Stuiver, 1975). Care must be taken when using $\delta^{13}C$ to deduce information concerning climatic or other changes considering that many factors may be involved (Håkansson, 1985).

Interpretation

Other geochemical parameters measured on the Monticchio profile (C, C/N, BSilica, HI) appear to be related to the stable carbon profile in *certain* areas, and this suggests that source changes are at least partly responsible for the isotopic variations. From Fig. 4.18. there appears to be a negative correlation (r=-0.625) between $\delta^{13}C$ and C/N ratio over the 3000 and 4700cm depth region. This may be due to an increased contribution from higher C3 plant organic matter with light isotopic values (-30‰?) mixing with isotopically heavier (-22‰?) planktonic lacustrine matter in the zone between 3300 and 3400cm depth. In addition, greater degradation of the organic matter between 3500 and 4700cm depth could have caused preferential loss of ^{12}C leading to higher $\delta^{13}C$ in the remaining organic matter.

The $\delta^{13}C$ record for the upper 1000cm is shown together with other geochemical parameters in Fig. 4.21. The section between 950 and 750cm, displaying an isotopic shift towards lower values, cannot be correlated with the biogenic silica or hydrogen index profiles which both remain fairly constant over this interval. Also, it is difficult to correlate the small $\delta^{13}C$ minima zone within this trend at 895 to 925cm with any other geochemical information. There is a temporary positive correlation with organic carbon and C/N ratio, but only in the subzone between 820 and 700cm depth. The positive correlation here between $\delta^{13}C$ and C/N ratio contrasts with the inverse relationship seen at 3300cm depth. It is planned to investigate this zone of pronounced isotopic shift with the aid of compound specific isotope ratio mass spectrometry in the hope of revealing additonal information (e.g. Rieley et. al., 1991).

During the Holocene period itself there is a good correlation between $\delta^{13}C$ and the ratio of organic carbon to biogenic silica (Fig. 4.21.). From the C/N ratios it has been suggested that

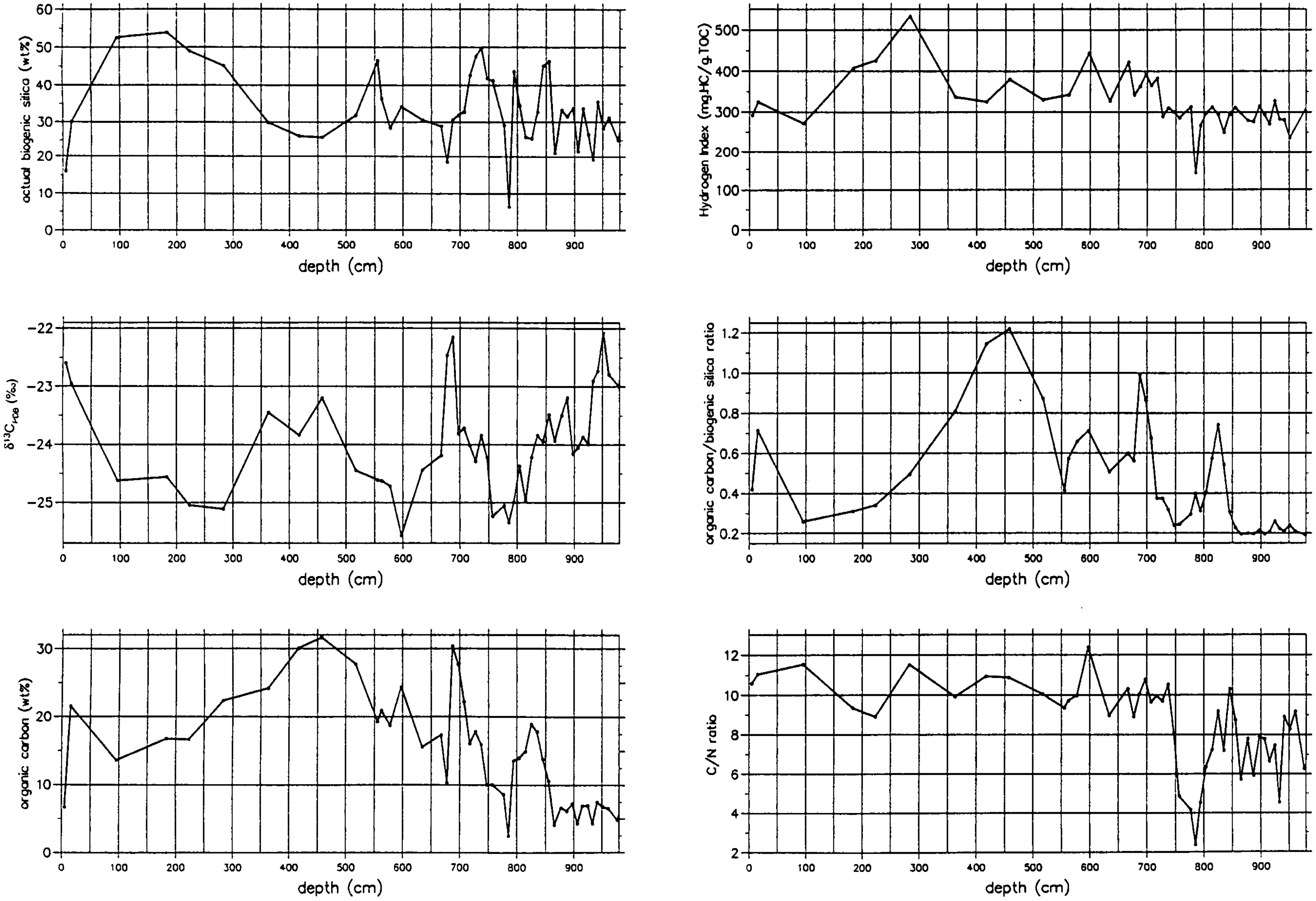


Fig. 4.21. Comparison of bulk geochemical parameters for the upper 10 metres of record

this period experienced consistently high contributions from autochthonous productivity and that the major changes in organic material are due to the relative dominance of diatoms and other types of algae. It is possible that the diatom organic matter component has a lighter isotopic composition (-28‰?) than the averaged ratio of the non-diatom algal matter component (-22‰?) and that the isotopic profile is mainly shaped by the mixing of these sources. Isotopic measurements made on recent aquatic components in Lago Grande would aid this interpretion. Nevertheless, the section between 650 and 500cm depth departs from this simple correlation and it is noted that a brief maximum in C/N ratio occurs at 600cm depth in parallel with a minimum in $\delta^{13}C$. This might suggest that a temporary increased contribution from isotopically light higher plant material may be causing a greater influence at this time. It is also possible that the sharp rise towards heavier $\delta^{13}C$ at 700cm, associated with a sharp presumed rise in productivity (organic carbon), could reflect some influence from a decrease in the effectiveness of kinetic fractionation and the formation of higher $\delta^{13}C$ values in the aquatic carbon photosynthesised.

Between 1000 and 3000cm depth the isotopic values hover around -24‰ and the lack of change makes it difficult to extract information from this zone. A number of positive excursions occur, for example at 1400cm depth. Although a number of horizons rich in macrophyte plant material (which may include submerged and isotopically heavy types) have been noted in the sequence, none of these appears to be associated with the excursions seen. Carbonate sediments, however, occur throughout this section and it is possible that periods of increased water hardness could have influenced the photosynthesis of some of the submerged plant matter (Håkansson, 1985) and caused isotopically heavier organic matter to be deposited at certain times. This could again be tested for by using compound specific isotope measurements to see whether the terrestrial organic matter has also experienced $\delta^{13}C$ enrichments at these times.

The lack of a simple or coherent interpretation regarding the $\delta^{13}C$ record could reflect the lake's insensitivity to direct climatic change, although the two pronounced shifts observed may disprove this if they can be fully understood. The lake's location in a moderately elevated Mediterranean climatic zone must bear some responsibility for its behaviour. Perhaps the vegetation associated with some of the northern European sites suffered more climatic stress between glacial and interglacial periods. It is also possible that autochthonous organic matter is profoundly influenced by the lake water bicarbonate reservoir. This could modify the expected ratios if a majority of plants are assimilating carbon from this source and changes have occurred in the lake water chemistry. For example, the lake waters may have been altered during periods of carbonate precipitation or through volcanogenic CO_2

emissions at certain time periods. Also the possibility that a significant fraction of the organic matter may consist of reworked material which is not reflective of the environmental conditions at the time of depostion could be responsible for further confusion in the signal. These results emphasise the local differences between individual lakes and the difficulties of investigating bulk organic matter.

CHAPTER 4b

TERRIGENOUS CLASTIC COMPONENTS OF THE SEDIMENTS

Introduction

Examination of the terrigenous mineral component should provide physical and chemical information on the sedimentation regime. Grain size and mineral distribution may be related to physical processes of erosion and transportation while mineralogy and chemistry are connected with source and the amount of mineral alteration that has taken place. It is again emphasised that the chemical elements measured reside in discrete mineral phases and that the nature of these phases must be characterised to fully appreciate the sedimentary processes operating. Although some basic sedimentology and mineralogical information is known, most of these studies are yet to be carried out by other institutions working on the Monticchio record. At the moment quantitative information on subjects such as particle size distribution and clay mineralogy is not available and this imposes some limits on the geochemical interpretation.

MAAR SEDIMENTATION

One of the first detailed studies concerning sedimentation in a volcanic lake was made by Nelson (1967). Crater Lake (Oregon) is actually a relatively large caldera lake, but has many similarities with maar environments. The lake itself is at a young stage of development and is dominated by mineral clastic sediments and nutrient-poor conditions. It was recognised that the lake sediment mineralogy (plagioclase feldspar, pyroxene, hornblende etc.) was very similar to that of the surrounding bedrock suggesting a strong relationship between local source supply and sedimentation. Poorly sorted deposits of fine material were related to the low energy introduction of sediments into the lake by wind action, wave erosion or surface creep. On the other hand, well sorted sand and silt layers were related to turbidity currents.

White (1989) proposed a general development model for maar-crater sedimentation based on studies from semi-arid regions. After the initial 'excavation event', early sedimentation would be dominated by slumps and debris flows. However, as the environment became more stabilised (perhaps through slope reduction or the binding effects of vegetational development), laminated sedimentation would take over. In the final stages this might be interrupted by ingression of external fluvial systems or of aeolian depositional systems. In the semi-arid playa setting studied the laminated sedimentation consisted of carbonate deposits, but it was suggested that under different climatic and/or groundwater regimes the sedimentation type would be different during this stage.

In South Africa, Smith (1986) recognised three depositional facies in an ancient crater-lake deposit and equated 'normal' lacustrine sedimentation with the laminated mud facies. This was thought to have accumulated through the settling of fine material from suspension under possible seasonal influences. Within the microlaminated muds incursions of turbidites and tephra layers were observed, while in nearshore areas pyroclastic talus cones and debris flows occurred (Fig. 4.22.).

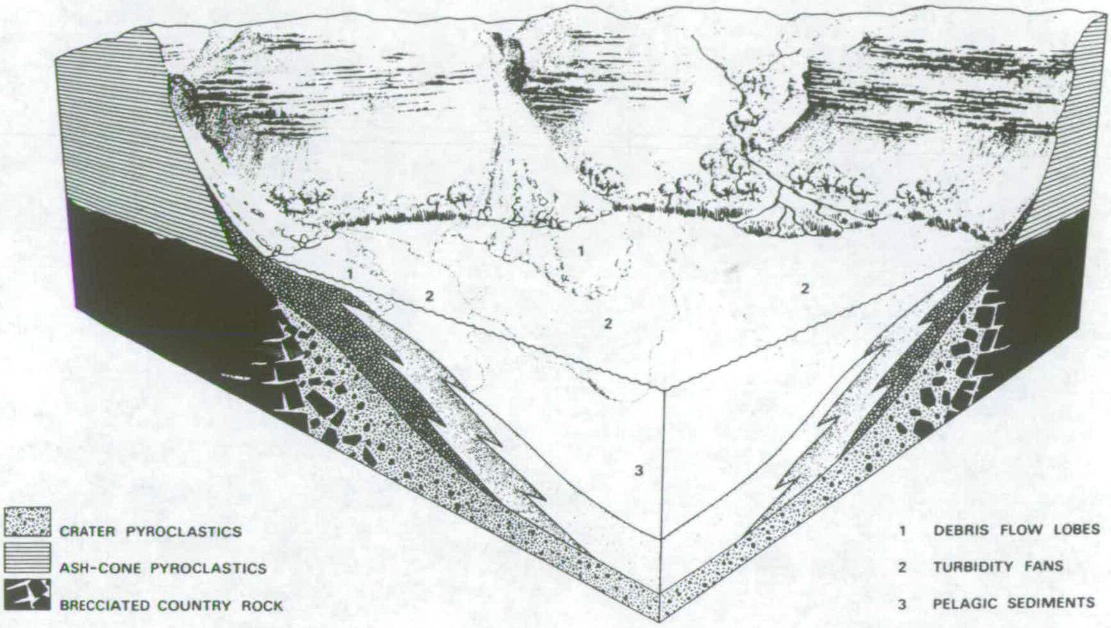


Fig. 4.22. Depositional facies in a crater lake (modified from Smith, 1986)

Comparable features are found in sedimentary sequences from the Eifel maar region in Germany (Negendank et. al., 1990). Here the Holocene record is characterised by organic varve deposition incorporating thin clay layers which have settled from suspension. During glacial times when reduced vegetation cover permitted greater catchment erosion, silt-clay laminae or thin turbidite layers are more common. Coarser layers of sand material are related to tephra inputs such as the well known Laacher See Tuff horizon.

In Lac du Bouchet, Truze (1990) found that during vegetated interglacial periods sedimentation was also dominated by quiet-water clay settling. During periods of reduced vegetation cover the inwash of increased amounts of catchment material was related to possible high-rainfall periods causing rapid surface runoff. Changes were identified in the

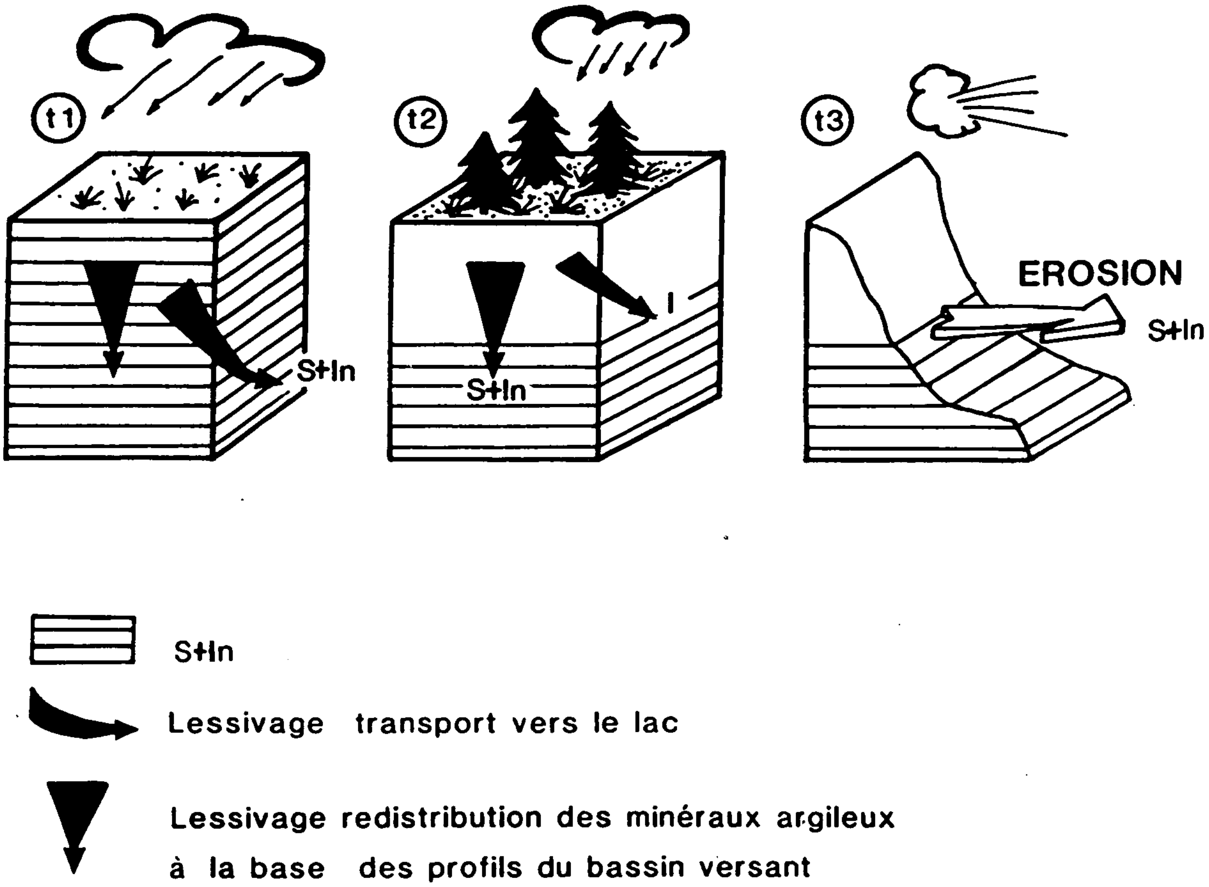


Fig. 4.23. Model for clay mineral evolution in catchment soils based on Lac du Bouchet (Truze, 1990)

t1) inwash of smectite (S) and 'interlayered' (In, mixed layer) clays during the early stages of a temperate/interglacial period,

t2) downward migration of smectite and interlayered clays during the main interglacial phase. Illite (I) and kaolinite (K) which become dominant in the upper parts of the soil profile are transported to the lake,

t3) during the subsequent cold/glacial period erosion causes widespread removal of surface soil layers. Smectites and interlayered clays reappear in the lake sedimentation clay mineralogy too. The catchment soils had been observed to contain mainly illite and kaolinite in their most weathered surface horizons, but increasing quantities of smectite and interlayered clays with depth. The soil profile was also judged to have remained of similar composition throughout the history of deposition. During temperate vegetated periods the slightly higher illite and kaolinite concentrations in the lake sediments were related to the gradual removal of surficial soil layers into the basin. During more active erosional periods (evidenced by coarser sediment grain sizes) the increased content of smectite and interlayered clays was attributed to the deeper incision and removal of soil layers (Fig. 4.23.).

Like most maar-lake studies these interpretations have involved the assumption that changes in the sediment mineralogy are primarily due to changes in the weathering and erosive regime acting on minerals from within the catchment -i.e. that the catchment is the dominant supplier of material. In some studies the presence of probable aeolian material, such as rounded quartz, has been noted but rarely quantified. In most settings, however, it would be unlikely that this has had a major influence on the clay record and that, excluding continued inputs from external tephra fall, the terrigenous minerals reflect the catchment source zone.

SEDIMENTOLOGY AND MINERALOGY

Basic indications of the sedimentology at Monticchio are apparent from visual inspection of the core sections (c.f. Fig. 2.4. and Plates 3-5.). Most of the sediment sequence is relatively fine grained consisting of muds with various amounts of organic material present. Only in the tephra horizons and in the zone of turbidites around 20 metres depth do the sediments contain sands or coarser clastic material.

Preliminary XRD mineralogical investigation by Irion (unpubl. work) has found very low concentrations of clastic minerals over large sections of the profile, particularly between 0 and 660cm and between 3200 and 3500cm depth. This is due to dilution by the large amounts of organic matter and amorphous silica present and makes detailed identification of the clay mineral assemblages difficult. A similar situation exists in certain other volcanic lakes, for example Lake Kivu, where clay minerals were undetectable in a diatom-rich facies (Degens et. al., 1973).

The present author has found evidence for members of the illite-muscovite clay group $KAl_4[Si_7AlO_{20}](OH)_4$ and perhaps also halloysite $Al_4Si_4(OH)_8O_{10}.8H_2O$ and beidellite $(Ca,Na)_{0.7}(Al,Mg,Fe)_4[(Si,Al)_8O_{20}](OH)_4.nH_2O$ from XRD examination of trial sediment

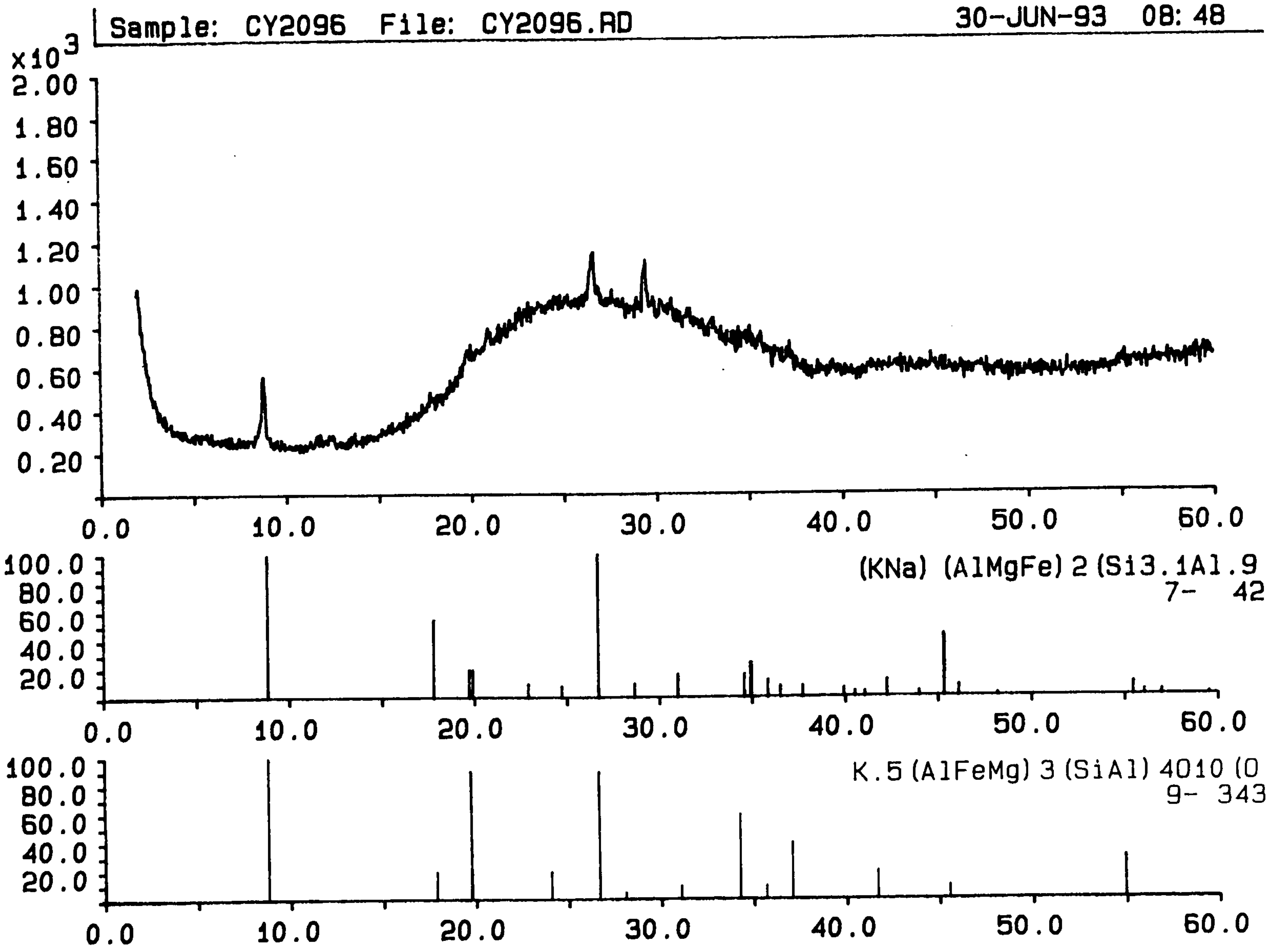


Fig. 4.24. XRD trace for a clay suspension taken from 2096cm depth

(reference patterns for muscovite and illite shown for comparison)

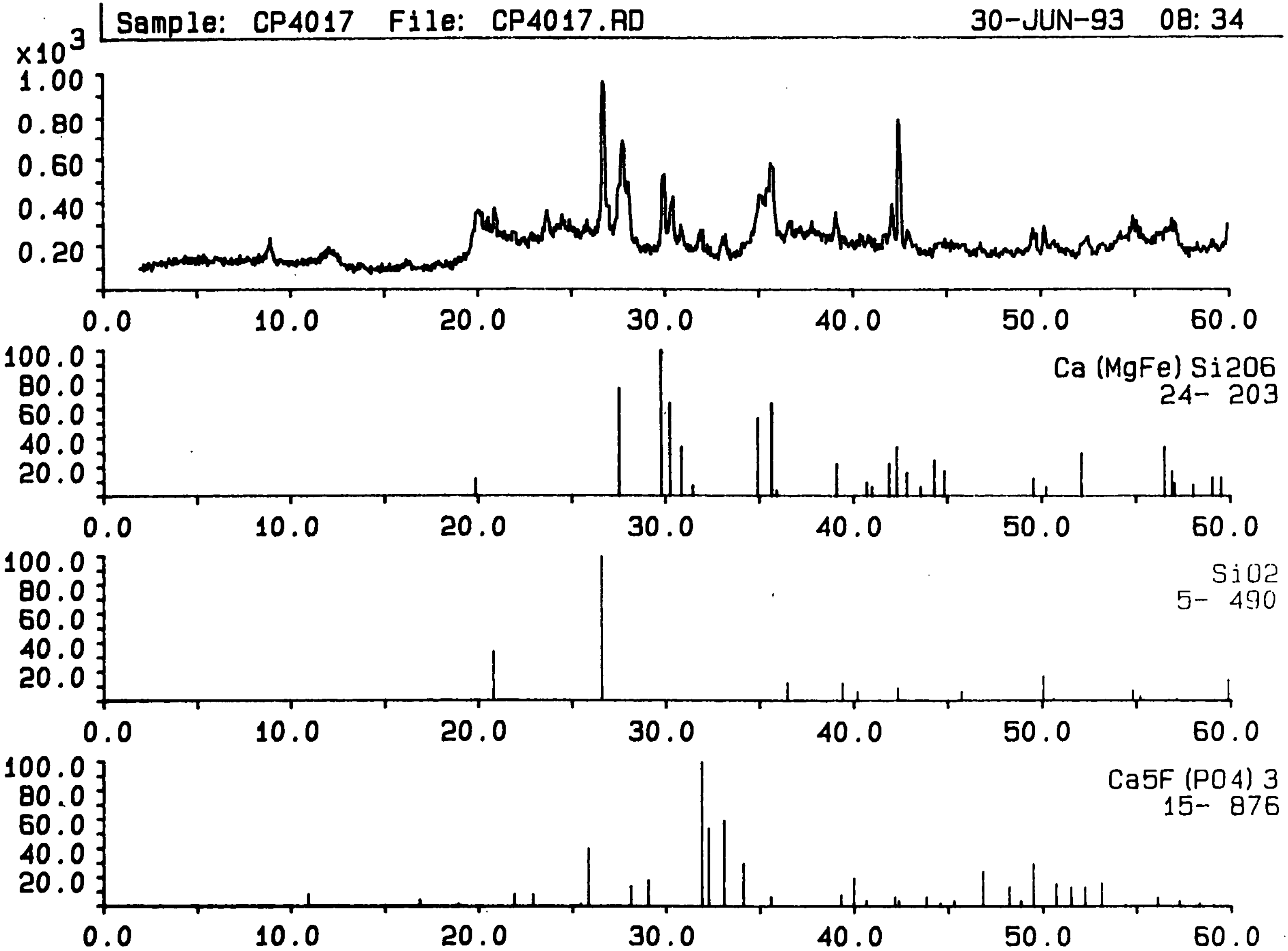


Fig. 4.25. XRD trace for a sample taken from 4017cm depth

(reference patterns for augite, quartz and fluorapatite shown for comparison) suspensions. Fig. 4.24. illustrates the diffraction trace for a clay suspension taken from a sample at 2096cm depth. Prominent in this trace is the illite/muscovite peak at 8.8° and a large hump feature between 20 and 35°. Irion (unpubl. work) also reports illite, together with kaolinite and smectite, to be present in 'small amounts' and recognises a pronounced hump zone around 4.5Å which is related to amorphous substances. These may include diatom silica, volcanic glass and amorphous clay minerals. Amorphous clays such as imogolite ($SiO_2.Al_2O_3.2H_2O$) and allophane ($1.0\text{-}2.0SiO_2.Al_2O_3.2.5\text{-}3.0H_2O$) are known to occur in volcanic weathering regimes (Wada, 1987) and could represent a significant fraction of the clay mineral assemblage. A proper investigation of the clay mineralogy will require careful preparation techniques and additional analyses steps including infrared spectroscopy in order to place some quantitative value on the mineralogical changes. This would ideally be accompanied by a survey of soil profiles from the present Monticchio catchment.

XRD examination of the bulk sediment shows that the main minerals present are pyroxene, quartz and apatite. These are probably concentrated in the silt fraction and are illustrated in Fig. 4.25. which shows the XRD trace for a sediment sample from 4017cm depth. It is thought that pyroxene and apatite are locally derived and survive weathering processes in preference to the feldspathoid and glass components of the local rocks. These latter phases are known to be rapidly decomposed by reactions such as hydrolysis (Loughnan, 1969). Quartz is considered to be exotic to the Vulture petrological system, but has nevertheless been recognised in mineralogical studies (Fiore et. al., 1992). It may have been acquired during magma ascent and be present as xenocrysts. Due to its strong denudational resistance and its over-representation on XRD traces (G. Angell, pers. comm.) its appearance is emphasised during the mineral identification. Some quartz may also be of aeolian provenance, but this cannot be confirmed without examination of the grain morphologies under high magnification.

Tephra layers also contain considerable pyroxene and apatite together with alkali feldspars (sanidine and orthoclase), plagioclase and some leucite. Several of these tephra layers have been defined as trachytes from analysis of their glass fragments (Newton and Dugmore, 1993) and this is in fitting with the mineral assemblages observed.

PREDICTED SEDIMENTATION PROCESSES

The majority of the Monticchio sediment profile, which consists of finely laminated muds, probably accumulated through the gradual removal of soils from the catchment by wind action, surface creep or runoff and subsequent deposition by suspension settling. *Some* of the clay layers may also reflect the deposition of distal turbidites (B. Zolitschka, pers. comm.). This accumulation would be augmented by an unknown amount of aeolian transported material and by deposition of biological matter produced within the lake. The turbidite layers, most noticeably between 1900 and 2200cm depth, contain silt or fine-sand material and reflect more energetic depositional processes. They could be generated through the instability of quantities of sediment in the crater region or in littoral areas, perhaps triggered by heavy rainfall or seismic activity. Such events are more likely to occur when vegetation cover is reduced, as during glacial periods. The tephra layers, which often present distinct horizons, result from the direct airfall of volcanic material into the lake and the lesser effects associated with secondary catchment inwash following the depositional event.

Thus there appear to be three sources of clastic material to the Monticchio sediments: 1)local catchment minerals (both primary and secondary), 2)tephra inputs and 3)aeolian material which may have been transported over long distances. Under normal circumstances the local catchment supply would be expected to dominate a lake's sedimentation, but if catchment material is supplied at a very low rate, the external sediment sources might have a primary influence on the mineralogy observed. To some extent the contribution from tephra falls can be recognised in the form of prominent and discrete horizons, but the effects of secondary inwash cannot be accurately assessed with the sampling resolution of this study and it is possible that a number of minor tephra-fall events have contributed to the sediments without being readily visible. Aeolian dust is unlikely to contribute large accumulations of material in the absence of local dune systems, but in the deep marine environment it has been shown that dust contributions (from the Saharan desert) can account for most if not all of the clastic sediment component (Prospero et. al., 1981). This results from the otherwise **extremely** low sedimentation rates in such an environment.

It would be desirable to retrieve information from the sediment record concerning the individual inputs from these three components **and** concerning the changes in the catchment weathering-erosive regime, if possible. It is often difficult, however, to separate out the signals from provenance and weathering regime by geochemical means (Fairchild et. al., 1988). Also, with the mineralogical information available it is not possible to constrain the relative importance of these three sources reliably. In theory, it might be possible to use trace mineral assemblages as signatures for the different source provenances, but there may still be too much overlap in the mineralogy to separate the three components. In terms of the geochemistry, many elements show considerable overlap between different phases. Potassium, for example, may be contained in alkali feldspars (strongly associated with the tephra horizons), but also in feldspathoid minerals and in illite which could both be derived from the catchment area *or* externally. Interpretation of the geochemistry will be made in the light of the mineralogical and sedimentological information that is available and by making deductions concerning the most likely host phases responsible.

GEOCHEMISTRY OF THE CLASTIC FRACTION

In Chap. 3 it was suggested that elements associated with the terrigenous clastic fraction were identifiable from the PCA data summary by their high negative loadings on the PC1 axis (Fig. 3.3. and Fig. 3.5.). It can be seen from these plots that many of the metallic elements are grouped within this field, although a number of metals exhibit intermediate behaviour between the inorganic and biological poles and show susceptibility to diagenetic mobilisation. In studying the clastic mineral fraction it is desirable to avoid additional imprints caused by diagenesis as these processes will be studied in their own right in Chap. 4c. With this aim, the current discussion will focus on the more conservative elements in the sediment system such as Al, Zr and K which are associated almost exclusively with the terrigenous clastic fraction, and do not become later involved in diagenetic processes. Elements such as Fe, Ca and P which *do* have a component in the clastic fraction, but are more complex because of their residence in diagenetic phases will not be focused on. Also, *many* of the trace elements analysed show similar behaviour to the major elements, but cannot be related to any single mineralogical phase with certainty. Their ranges of possible substitutions do not permit the bulk results to be interpreted with particular environmental significance beyond that provided by the major element data.

TOTAL AMOUNTS OF CLASTIC MATERIAL

Basic concentration profiles for conservative elements such as Al and Y (Fig. 4.26.) indicate how the relative amount of clastic deposition has varied. These elements show strong inverse trends to those elements reflecting biological sedimentation. For example, the correlation coefficient between Al and [organic carbon+biogenic silica] is -0.951.

The Holocene period is characterised by low values for these clastic indicators (Fig. 4.26.), although tephra layers within this zone add positive spikes to the underlying trend. A minimum seems to occur during the early Holocene between 750 and 500cm depth, above which values rise to slightly higher levels.

Clastic content rises sharply below 750cm depth producing a brief maximum in what may be the Younger Dryas period. After a subsequent minimum around 825cm depth, values rise

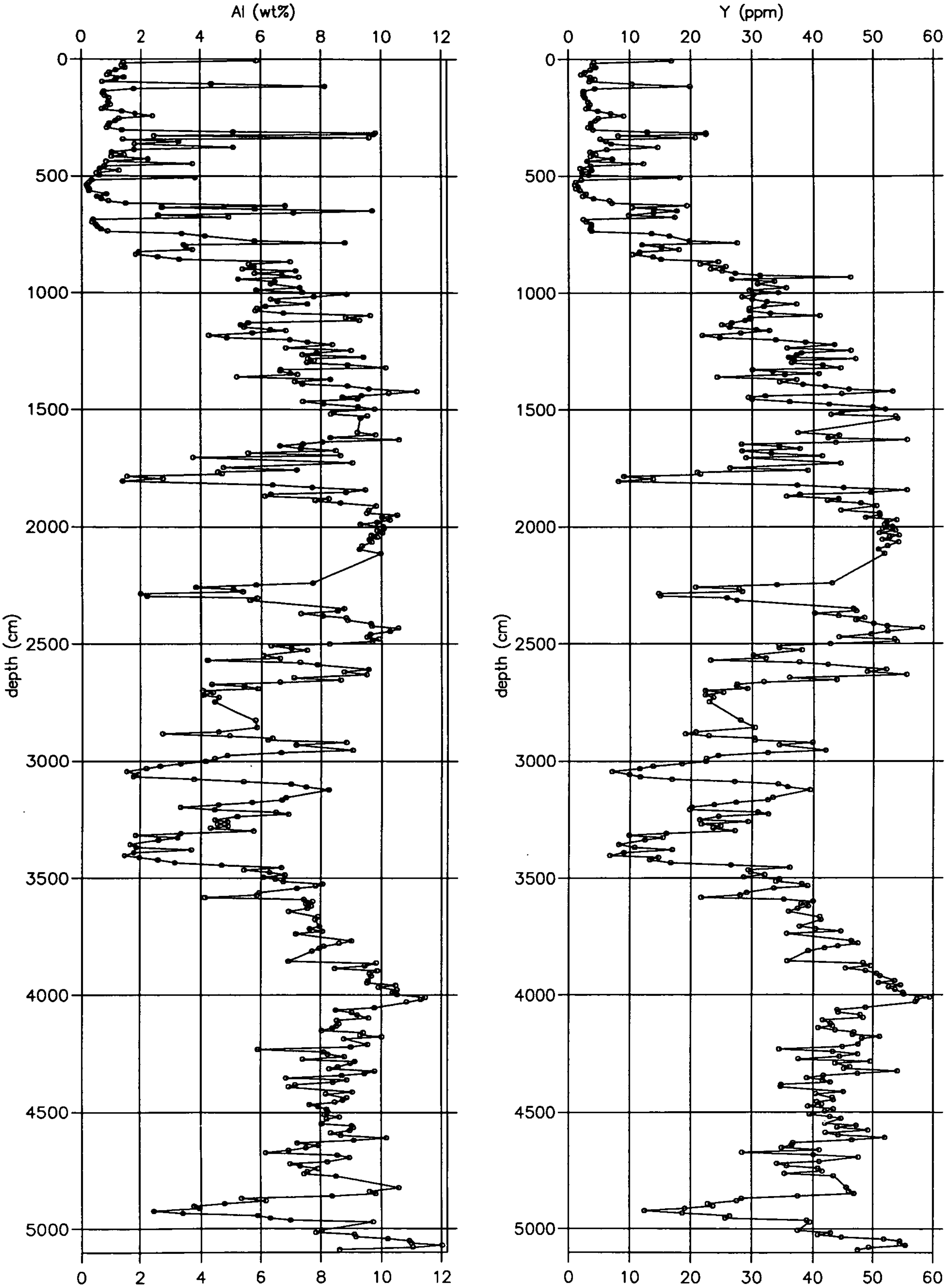


Fig. 4.26. Al and Y content

sharply again to much higher levels over the next 150cm. Maxima are reached at around 1500cm depth and lower in the profile at 2000cm, 2400cm and 4000cm depth. In these areas the concentrations of Al and Y are around x10 that in the Holocene. Prior to the Holocene, values never drop back to such a minimum, although pronounced minima occur at 1750cm, 2300cm, 3100cm, 3350cm and 4900cm depth. These zones have been previously related to interstadial or interglacial events depending on the age interpretion applied to the sequence (Chap. 3 and Chap. 4a).

Interpretation

Decrease in the clastic content of the sediment could be interpreted as reflecting reduced clastic deposition (i.e. diminished erosive and transportational processes) or dilution from increased biogenic sedimentation. This can only be determined objectively with accumulation rate data. It is possible that both effects may be operating simultaneously. For example, during the Holocene increased vegetation cover could stabilise the catchment slopes reducing erosive activity and at the same time permit more nutrient supply by leaching which would lead to increased organic productivity. Most of the sediment sequence consists of muds which contain fine laminae (<1mm in thickness) and it is thought that in such sections the rate of terrigenous inwash has not changed dramatically. Therefore the primary factor causing change in clastic content is believed to be the dilution effects from dramatic increases in biological productivity. However, the tephra layers and the relatively coarse turbidites at 2000cm depth (which sometimes contain laminae over 10mm in thickness) probably represent situations where enhanced clastic deposition represents the primary control.

NATURE AND QUALITY OF THE CLASTIC MATERIAL

Due to the large mutual dilution effects between clastic and biogenic components it is necessary to compensate for changes in the biological content of the sediment in order to examine changes within the terrigenous mineral fraction. Mackereth (1966) looked for element changes within the ash fraction which had been produced after ignition of the total sediment. The geochemical data from Monticchio may be examined in this way since major elements were analysed from the ignited fraction produced during XRF fusion. However, in Monticchio significant amounts of *biogenic* silica are present in this fraction and trends attributable to changes in the clastic mineralogy could still be obscured. Therefore it is best to examine ratios between elements which are neither influenced by the organic matter component nor the biogenic silica component. It is common practise to ratio other elements to Al which is relatively abundant and considered to remain essentially constant during sedimentary processes (Krauskopf, 1967).

Na/Al RATIO

The Na/Al ratio has been used as an index of weathering in lake sediment studies (e.g. Dean et. al., 1984). This approach assumes that during periods of increased weathering intensity greater amounts of alkalis are leached from the catchment soils and therefore material with lower Na/Al ratios is deposited into the sediment. Conversely, when erosive processes dominate over weathering, sediments are deposited with more of the alkali elements 'locked' in the mineral lattice. An alternative hypothesis to the weathering index or 'record of changing soil compositions' idea is the possibility that soil profiles remain essentially constant in chemical composition for long periods of time. In this case a change in Na/Al or other ratios would reflect a 'mechanical sorting' effect caused by erosion to different depths into the same soil system or selective transport of sediments in different particle size classes (Dearing, 1991 and refs. therein).

Mackereth (1966) pioneered the first of these hypotheses in his examination of the Na content of the mineral (ash) fraction in Lake District sediments. This might be expected to reflect similar trends to the Na/Al ratio in the absence of biogenic silica. He found a positive correlation between this and the total amount of mineral matter in the sediment. During the glacial periods rates of erosion were high and so alkali bearing mineral grains were washed into the lakes relatively unaltered. The sediments from these periods possessed both high total mineral contents and high amounts of Na in the mineral fraction. In contrast, during post-glacial times erosion rates were lower and weathering processes operated more effectively causing small quantities of Na-leached mineral matter to be deposited. From the maar sedimentation model suggested by Truze (Chap. 4a) it might be expected that the Holocene sediments at Monticchio would exhibit lower Na/Al ratios than those from the glacial periods because weathering processes would be more effective over erosion during an interglacial period with increased vegetation cover. Although the soil *composition* might not change, it would be more likely that base depleted surface soil layers would be deposited since erosive processes would be weaker. Deeper erosive removal might be necessary to deposit layers of the soil zone retaining greater levels of alkali metals.

If the Na/Al profile is examined (Fig. 4.27.) it can be seen that the Holocene actually contains higher ratios (>0.1) than the preceding glacial periods. Tephra layers are alkali-rich in

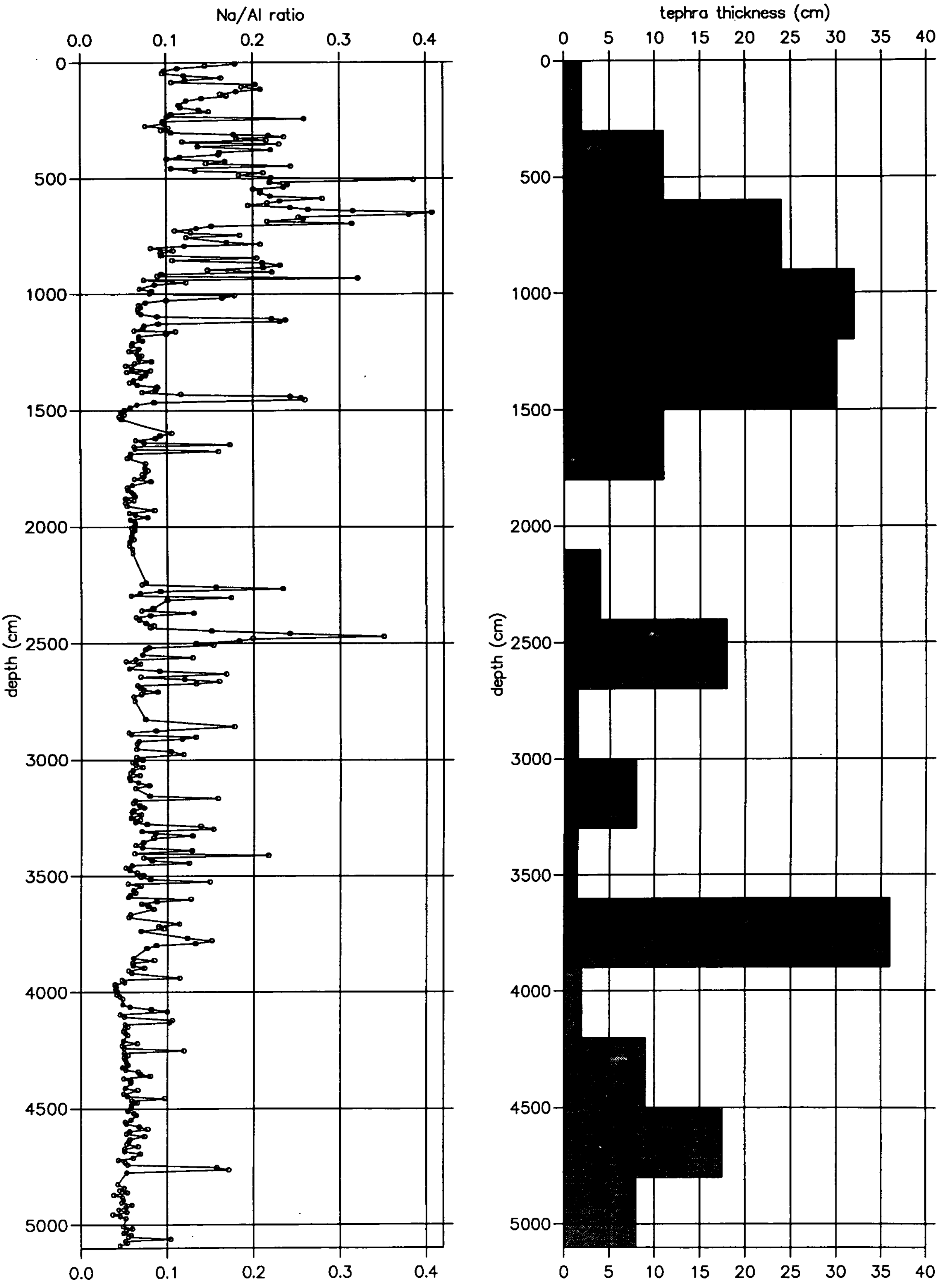


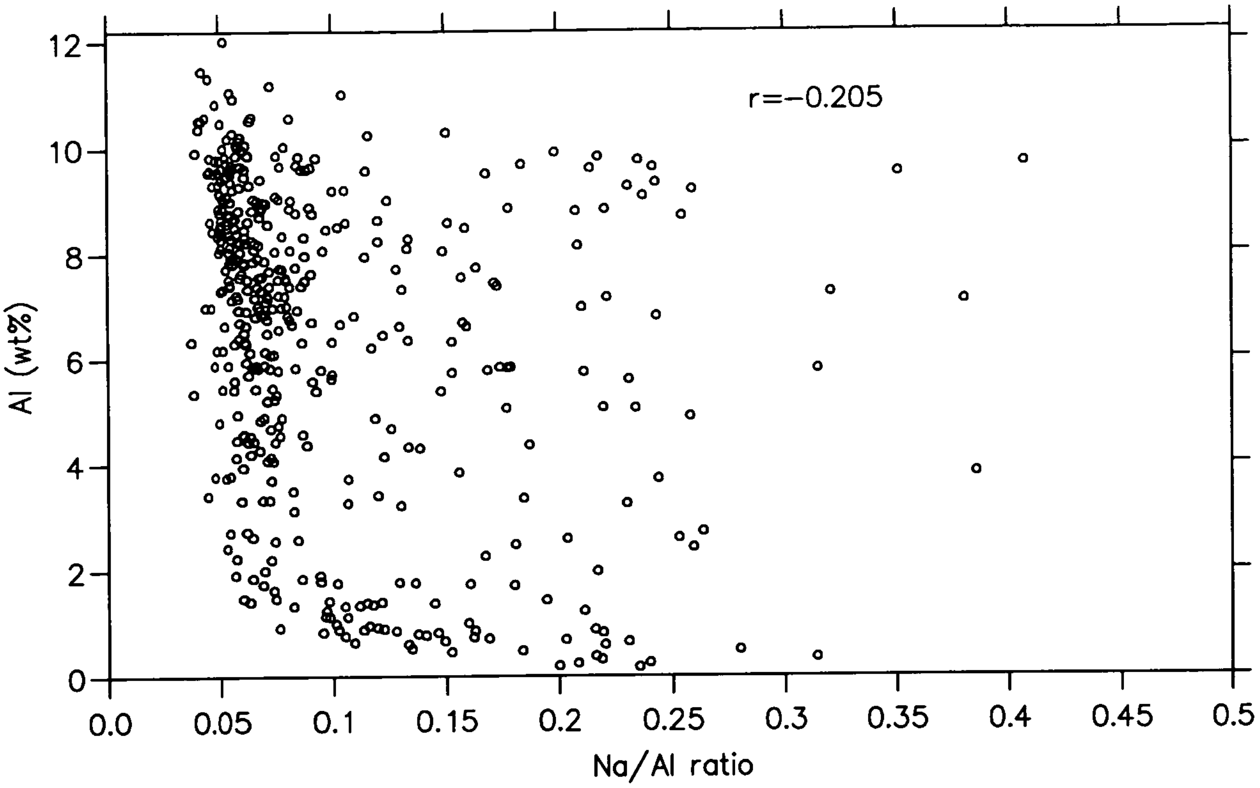
Fig. 4.27. Na/Al ratio and histogram of tephra thickness per 300cm of sediment

comparison with the normal sediments and impart positive spikes on the record. Much of the additional Na is expected to be hosted by alkali feldspar minerals.

If the profile is looked at in more detail it appears that Na/Al ratios around 0.05 are typical for the lowest part of the sequence between 5100 and 3900cm depth. Between 3900 and 3800cm values rise slightly and remain around 0.07 up until 1000cm depth. Above 1000cm Na/Al ratios increase further and remain consistently higher than 0.1. Tephra layers cause positive excursions towards 0.3 or 0.4, but values seem to remain elevated for prolonged periods outside the actual tephra horizons. For example, above a prominent tephra layer at 650cm Na/Al remains greater than 0.2 for the next 150cm (Fig. 4.27.). This suggests that the secondary deposition of tephra material supplied to the catchment might be responsible for the continued higher ratios in post tephra-fall sediments. Another possible example is found close to the shift in Na/Al values between 3900 and 3800cm depth. In this zone a thick tephra layer at 3815-3850cm occurs, although it is not included in the sampling and therefore cannot be seen directly in the geochemical profiles. A histogram of tephra thickness (in cm) per 300cm of sediment was compiled from visual notes. It is shown for comparison beside the Na/Al profile (Fig. 4.27.). This illustrates the major deposition of tephra between 500 and 1500cm in the record which corresponds to increasing Na/Al ratios seen in the sediment geochemistry.

Interpretation

A scatter plot of Al against Na/Al ratio should show a similar trend (i.e. a positive correlation) to the total mineral content against 'Na in the mineral fraction' plot used by Mackereth (1966) *if* there is a relationship between catchment weathering-erosive regime and the type of minerals sedimented. However, if the samples from Monticchio are plotted it appears that a weak negative relationship exists between the two parameters (Fig. 4.28.). It should be remembered that in this diagram Na/Al is a reflection of mineral quality and Al content is being used to represent the amount of erosion. This latter parameter would ideally be replaced with Al accumulation rate as it is possible that Al content changes do not always reflect increases in mineral erosion. Nevertheless, it would seem that possible signals from the catchment weathering-erosive regime are outweighed by the effects of tephra supply which has probably caused marked changes in the quality of mineral matter deposited. Under normal sedimentation conditions there is often little change in the Na/Al ratio that can be attributed to catchment weathering/erosion. For example, between 2500 and 3750cm depth relatively few tephra layers are observed and there is also little change in the Na/Al ratio from a value around 0.07.



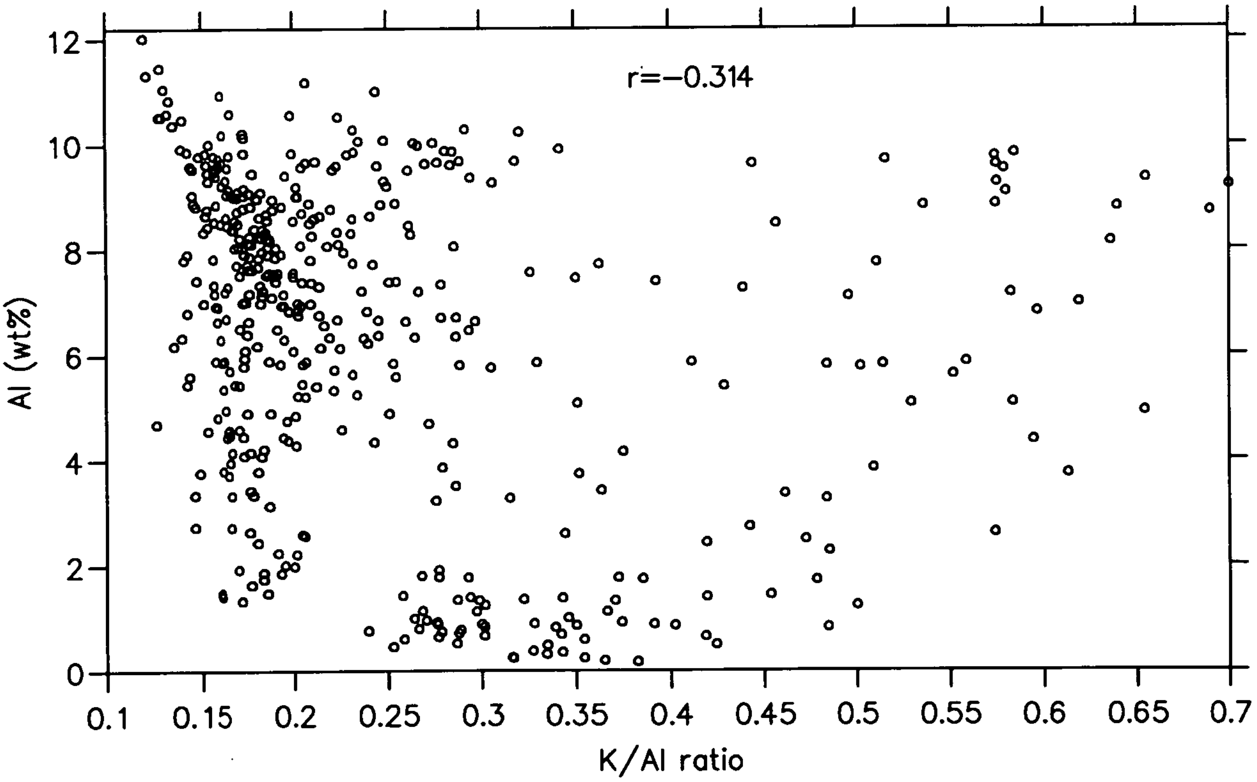


Fig. 4.28. Scatter plots of Al content against Na/Al and K/Al ratios
(all samples included)

K/Al RATIO

The K/Al ratio might be expected to show similar behaviour to the Na/Al ratio since both reflect the alkali metals group. Potassium was also used by Mackereth (1966) to deduce changes in catchment weathering-erosive regimes. If the K/Al profile is examined (Fig. 4.29.) it appears to follow a similar trend to Na/Al. The K/Al values are generally below 0.2 for the core section between 5100 and 1000cm depth and rise to >0.3 background values for the upper 1000cm. Tephra layers show prominent positive spikes and their increased K content is probably associated with alkali feldspar phases once more. As with Na/Al there appears to be no positive correlation between K/Al and Al content when the whole data set is examined on a scatter plot (Fig. 4.28.).

Although a similar interpretation to that for Na/Al is proposed for much of the record, it is noted that a prominent zone of elevated K/Al values occurs around 2100cm depth. This is in the region of mineral rich turbidites where the sediments are believed to contain increased concentrations of illite (Irion, unpubl. work). The elevated ratios in this zone are thought to be associated with the increased illite contents which may have been brought about by enhanced erosion and removal of deeper soil layers in the catchment region. This will be discussed further at the end of the chapter.

Mg/Al RATIO

Mackereth (1966) again associated the concentration of Mg in the mineral fraction of lake sediments with the degree of catchment weathering versus erosion. From the XRD examination of the Monticchio sediments and the mineralogy of primary igneous rocks in the catchment area (Chap. 2) it is believed that pyroxene represents the dominant host for this element. Therefore changes in the Mg/Al ratio may reflect the relative deposition of pyroxene together with possible changes in the degree of weathering.

Mg/Al ratios for the base of the core up to 1000cm depth are typically around 0.1 or 0.15 (Fig. 4.29.). Noticeably elevated values occur around 2100cm depth in the turbidite zone, suggesting that the turbidites contain relatively high concentrations of pyroxene. This geochemical change may be a consequence of chemical sorting through particle size effects (Dearing, 1991). It is likely that pyroxene is more abundant in the silt fraction of sediment sources and so if coarser material is deposited it will carry higher proportions of Mg within its constituents. The tephra layers, however, are characterised by negative spikes (e.g. at 2470cm and 1450cm) or by average values for Mg/Al. It is possible that many of the trachytic

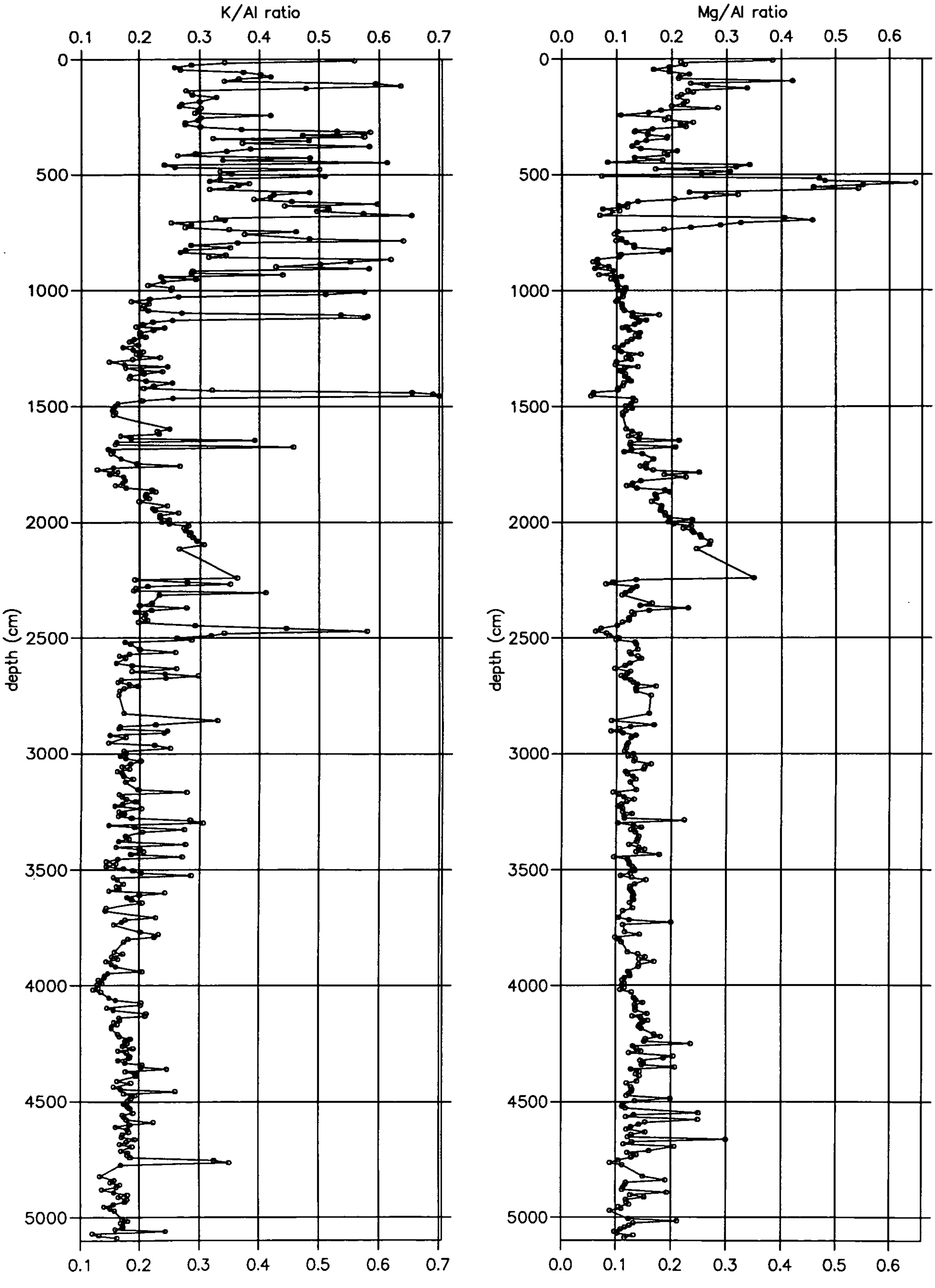


Fig. 4.29. K/Al and Mg/Al ratios

tephra possess relatively low pyroxene contents in comparison to the amounts of Al-bearing phases (e.g. feldspar) that they provide.

Between 1000cm and the top of the profile Mg/Al ratios generally range between 0.1 and 0.2, with higher values in the uppermost 300cm. Imposed on this trend are a number of much higher zones at 825cm, 700cm, 530cm and 460cm depth. In these zones Mg/Al ratios reach as high as 0.6 which is twice that in the turbidite zone maximum at 2100cm. These Holocene peak areas do not coincide with tephra layers, but are sometimes associated with high Fe and P concentrations. This relationship may result from limited amounts of diagenetic enrichment, for example substitution in an iron phosphate phase (Chap. 4c).

Ti/Al RATIO

The Ti/Al ratio may be associated with grain size variations in certain environments (Calvert, 1976). Ti is generally bound in minerals such as ilmenite and rutile which are concentrated in the coarse sediment fraction and so Ti/Al might be used to reflect the silt/clay content of the sediment. In Monticchio, these Ti-bearing minerals have not been identified in the sediments and, if present, are not thought to be abundant. It is considered more likely that most of the Ti resides in pyroxenes as with Mg. In contrast to Mg, however, Ti is a more residual element and might be expected to show less susceptibility to removal by weathering.

The Ti/Al profile shows that values around 0.06 to 0.07 are typical for the lower part of the core up to 1000cm depth. Slight maxima occur at 4250cm, 2150cm and 1250cm, although values rarely exceed 0.08. These maxima probably reflect higher contents of pyroxene in the sediments. Tephra layers are marked by strong negative spikes suggesting low concentrations of mafic or heavy minerals in these layers as compared with the surrounding catchment derived material.

The upper 1000cm of the profile generally exhibits lower values (between 0.4 and 0.6) with a minimum present at 700cm depth during the early Holocene. Enhanced supply of non-mafic material from the increased inputs of alkali tephra is probably responsible for the overall trend, although an association between the actual tephra horizons and negative Ti/Al spikes is not prevalent. There is a possibility that the Ti/Al maximum at 580cm depth may be connected with a diagenetic enrichment, but the relationship is not clear.

Zr/Rb RATIO

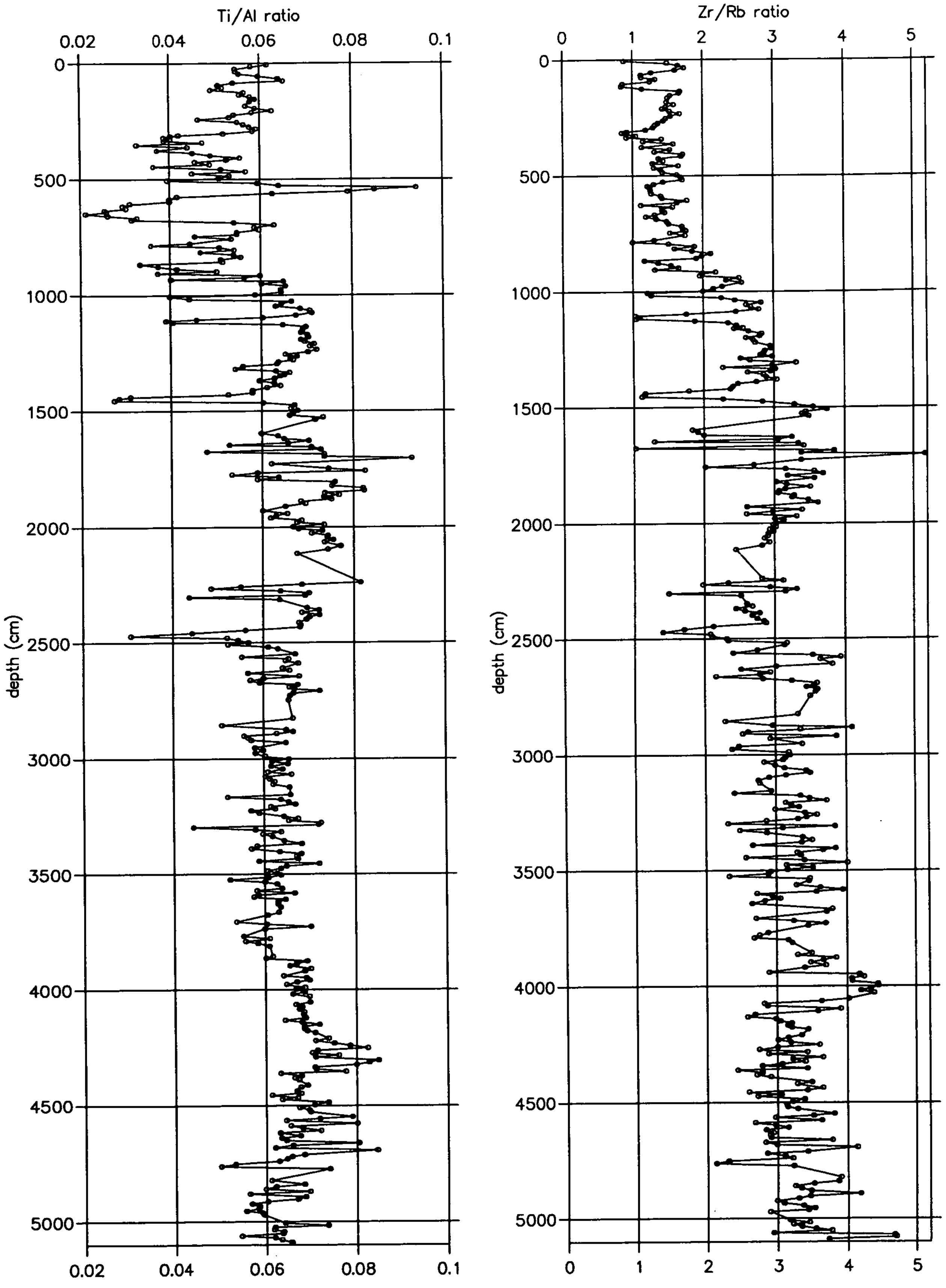


Fig. 4.30. Ti/Al and Zr/Rb ratios

The Zr/Rb ratio has also been used to identify changes in grain size (silt/clay) of the clastic material sedimented (O'Donnell, 1987). Zr is principally hosted by the mineral zircon which is concentrated in coarser sediments as opposed to Rb which might be concentrated in the clay fraction. In Monticchio it is possible that the Rb level could either reflect alkali feldspar content or perhaps alkali-rich clay components. Results (Fig. 4.30.) show that Zr/Rb ratios are relatively high (between 3 and 4) for the lower part of the core up to 1500cm depth. Between 1500 and 700cm values decrease progressively towards 1.5. From 700cm upwards the ratio remains steady at close to 1.5. Tephra horizons are marked by well-defined negative spikes.

There does not appear to be a primary relationship between Zr/Rb and grain size in this record. Firstly, the tephra layers which often represent coarse sandy material are characterised by negative spikes. Secondly, the zone of turbidites at 2000cm depth, which is significantly coarser grained than the surrounding muds, does not show an elevation above the average values for the lower core. Therefore it is thought that the Zr/Rb ratio primarily reflects the influence of external tephra inputs which are relatively rich in alkali elements as compared with the weathered catchment sources. Below 1500cm the tephra input events only cause a temporary drop in Zr/Rb ratios, but in the upper part of the record their effect would appear to be more pervasive. The transition between 1500 and 700cm could reflect a gradual shift towards catchment sedimented material which is compositionally influenced by a sequence of tephra falls that have progressively blanketed its slopes. The implications of this are that the entire catchment soil surface has altered due to tephra deposition. This would have consequences for the type of clastic material sedimented *and* possibly for the biological balance of the lake system (Haflidason et. al., 1992.)

FURTHER DISCUSSION

Catchment weathering

The catchment zone will comprise of a soil system containing primary and secondary minerals which rests upon primary igneous material below. A simplified model is illustrated in Fig. 4.31. The mineral distribution of a soil profile is unlikely to be uniform (Singer, 1980). Lower sections of the profile commonly contain more recently formed clay minerals which are at less advanced stages of weathering. The upper horizons where major leaching processes take place will contain secondary minerals reflecting the most advanced stages of weathering together with particularly resistant primary minerals.

It is predicted that the surface weathering horizons at Monticchio will be richer in components

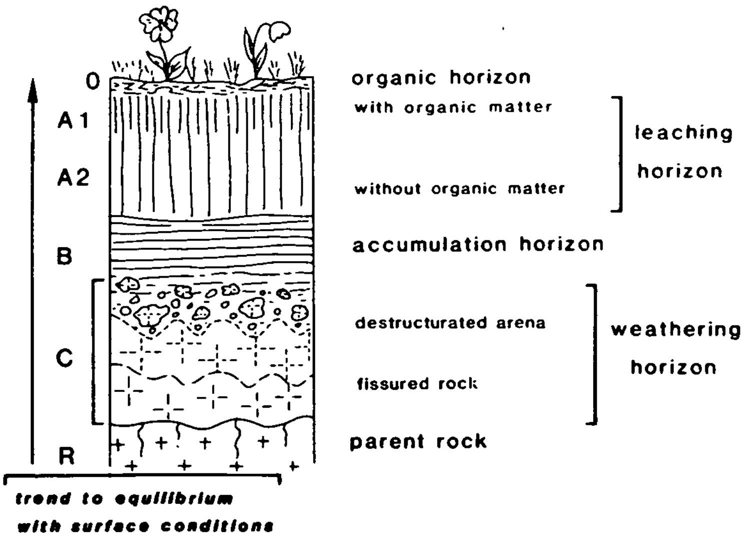


Fig. 4.31. A typical soil profile (Chamley, 1989)

such as allophane, halloysite, amorphous hydrous oxides and quartz due to intensive removal of K, Na, Ca and other ions. Deeper horizons would be expected to contain more illite, smectites (beidellite?), apatite and pyroxene. During normal depositional periods the lake sediments may have received material almost exclusively from the uppermost layers. Only during periods of major disturbance, such as when the coarse turbidite layers were deposited, would erosive processes supply material from the B and C horizons in quantity. Therefore the sediments are mineralogically dominated by amorphous phases together with small amounts of quartz and pyroxene for the majority of the record.

Under the criteria required if clays are to be used to reconstruct palaeoclimatic parameters (Singer, 1984) it would seem that the Monticchio sediment record contains significant overprints from the additions of volcanic material and from erosional changes perhaps induced by seismic activity (see following sections). These may alter the zonality of the catchment soil system and make a clear signal of climatic change inextractable.

Tephra falls

From the elevated Na/Al and K/Al ratios associated with tephra horizons in the record, it would appear that the tephra component that has fallen directly into the lake has not experienced substantial subaqueous losses through leaching. This is supported by the presence of feldpathoid minerals (e.g. leucite) and glass shards (Newton and Dugmore, 1993) in these layers. Timperley and Vigor-Brown (1985) constructed a whole-lake budget for major ions in the Lake Taupo system (New Zealand) and found that the major inputs of dissolved ions were derived from runoff, fluvial inflows, groundwater and geothermal waters. Somewhat enhanced concentrations of Na^+ in the sediment porewaters, however, were related to sub-aqueous weathering of pumice that had been introduced to the lake. This transfer was thought to be significant only in the upper 1cm of the sediment zone, particularly when the relatively coarse pumice layer had been covered with a subsequent layer of sedimented mud. Studies on the impact of the Mount St. Helens eruption (Wissmar et. al., 1982a; 1982b; Fruchter et. al., 1980) found large post-eruption enrichments of dissolved species in lakes which were in the immediate blast zone, but little change in the waters of more distant lakes which had received air fall material. Results suggested that the most profound impact on many lake systems would arise from catchment perturbation. It was predicted that the catchment zone would take a number of decades to recover while the lake itself was able to respond more rapidly. In Lago Grande di Monticchio it is probable that the tephra layers deposited on the lake bed have some direct influence on lake chemistry for a few decades at most before gradually becoming 'sealed' off by overlying mud layers.

The impact of a series of tephra falls on the Monticchio *catchment* could be to blanket a mature and highly leached surface horizon with layers of base-rich and unweathered material. This could favour improved vegetation growth in the catchment through improvement in the soil quality and soil-water retention (Mehringer et. al., 1977 and refs. therein). Rapid vegetational recovery might stabilise the newly deposited mineral layer and minimise erosion of the material into the lake sediments. In this case, the tephra deposits would gradually release chemicals to the lake through leaching action and presumably alter the lake chemistry. This could affect productivity if nutrient elements such as P and N were provided in greater quantity. Timperley (1983) found high P contents in the spring waters around Lake Taupo and attributed this to pumice dissolution. Change in the lake chemistry could also affect the diagenetic environment and the precipitation or dissolution of phases in the water column. For example, increased supply of Na^+, K^+ and Ca^{2+} ions from catchment weathering might promote the precipitation of calcium carbonate under conditions of increased alkalinity. These effects will be discussed in Chap. 4c.

It is concluded that the input of tephra material to the lake and particularly to the catchment zone could have profound consequences for the sediment record. These changes can be related to the model proposed in Chap. 4a which suggests that the more frequent inputs of tephra into Lago Grande di Monticchio during the later history of the lake are responsible for increased organic productivity in the system, a process which is independent of climate.

Aeolian contributions

The main present day sources of aeolian dust are shown in Fig. 4.32. The Sahara desert which lies to the south of Italy and the Mediterranean is considered to be the most significant contributor in of dust emissions in global terms. Mineralogical studies have shown that Saharan dust is dominantly composed of illite and quartz (Glaccum and Prospero, 1980) which are obviously minerals that coincide with the sediment mineralogy identified at Monticchio. The possibility of dust contributions from the Sahara and central Europe (e.g. the Alps) has been shown in sampling studies from the Adriatic and the Italian mainland. Tomadin et. al. (1984) observed higher concentrations of chlorite and ferromagnesian minerals in dusts of northerly provenance.

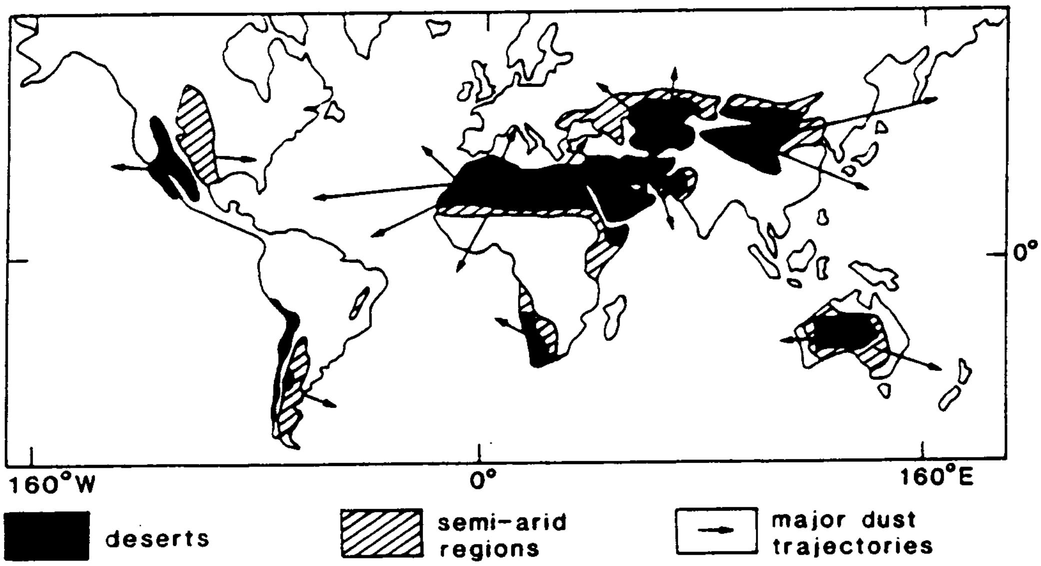


Fig. 4.32. Major present day sources of dust aerosol and dust trajectories (from Pye, 1987)

The relative significance of dust contributions is related to availability of source material (normally controlled to vegetation cover) and to wind patterns. Both of these factors are ultimately influenced by climate and in some instances it has been possible to correlate dust concentration profiles with global climatic records (Rea et. al., 1985). Dust accumulation can be very high (<1mm/year) in regions close to major dust sources, such as the loess regions of central China. On the other hand accumulations several orders of magnitude lower than this are more normal. Loÿe-Pilot et. al. (1986) estimated an average deposition rate of 0.01mm/year over the Mediterranean region from atmospheric trap studies. This compares with estimated lake sedimentation rates at Monticchio of between 0.12 and >1.0mm/year (Table 6.1.). It is therefore possible that aeolian dust may contribute a percentage of clastic material to the lake sediment record, but that in geochemical and mineralogical terms this may well be obscured by larger changes in catchment and tephra sediment contributions. Dust related clay minerals such as illite and chlorite are generally below detection levels except in the regions of most intense erosion where they reflect local weathering products.

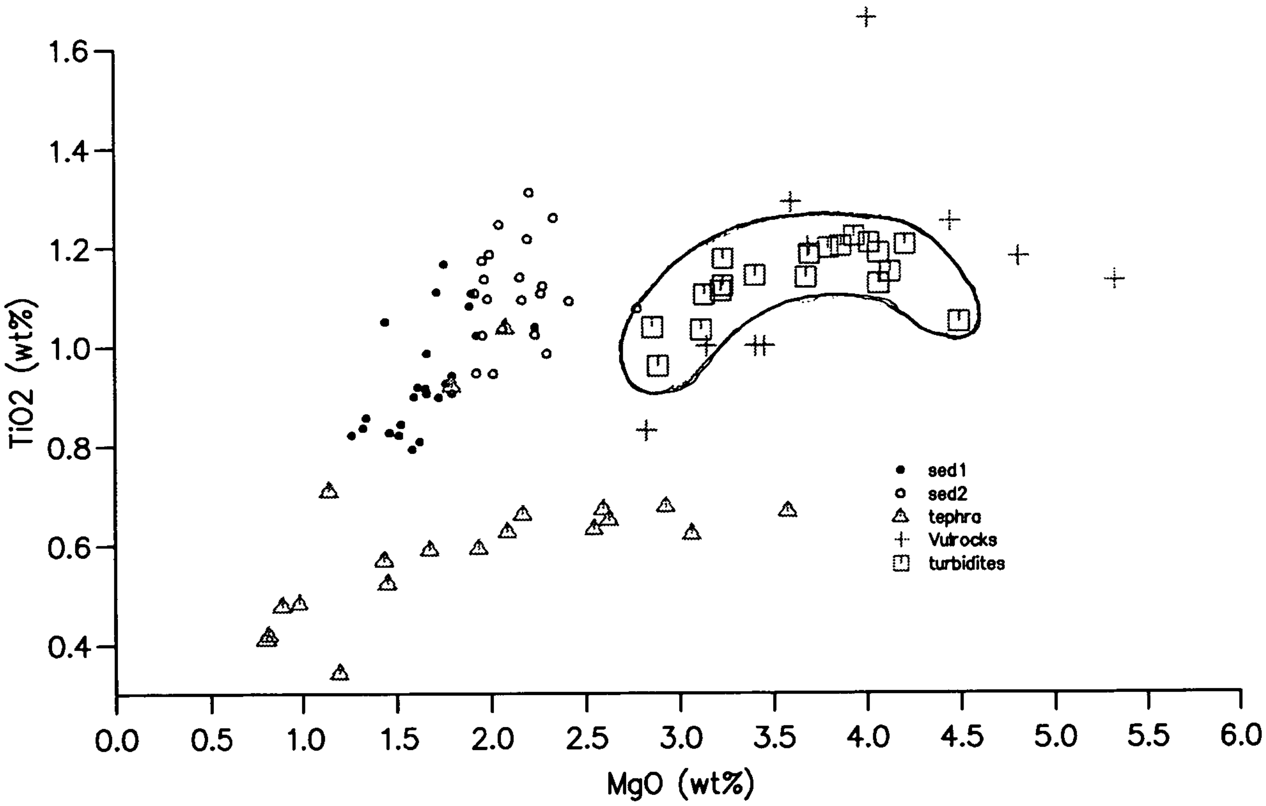
A few lake sediment studies have made indirect attempts to measure dust content. Work on Lake Ann (Keen and Shane, 1990) found a close relationship between the grain size and morphological distributions characteristic of aeolian material and magnetic susceptibility. The susceptibility profile was used to reconstruct a record of past dust deposition and this was interpreted in relation to regional climatic change. In the case of Lake Ann, local sand ridges are major feature of the lake environment and the amounts of dust sedimented by these were substantial. Seret et. al. (1992) used particle size measurements to reflect the dust content in the Grande Pile record. This is a lake/mire setting situated on an isolated watershed plateau where fluvial activity is absent. The silt content of the sediments was therefore considered to represent primarily aeolian dust and was used together with palynological data to reconstruct past temperature and precipitation changes.

It is concluded that for the Monticchio environment which has received relatively high inputs of tephra material and catchment sediments, the dust contribution is not a primary influence on the sediment geochemistry. It is not certain whether detailed sedimentological work would be able to identify a dust component, say of aeolian quartz and clays.

The turbidite zone

The zone of clastic rich sediments between 1850 and 2250cm depth represents an abrupt and pronounced change in lake sedimentation. Profiles of water content (Fig. 2.5.) and PC1 sample score (Fig. 3.6.) show abnormally low values for this interval before returning steeply towards normal background levels. Also the sediments contain almost no organic matter or diatoms in marked contrast with the finely laminated muds above and below. In addition to a series of turbidites, the 1850 to 2250cm zone contains a one metre thick slump horizon and below this a coarse sand layer (c.f. Plate 4.).

It was wondered whether this whole zone might reflect the input of an abnormally large tephra fall into the system, either from the trachytic source regions of Campania or perhaps



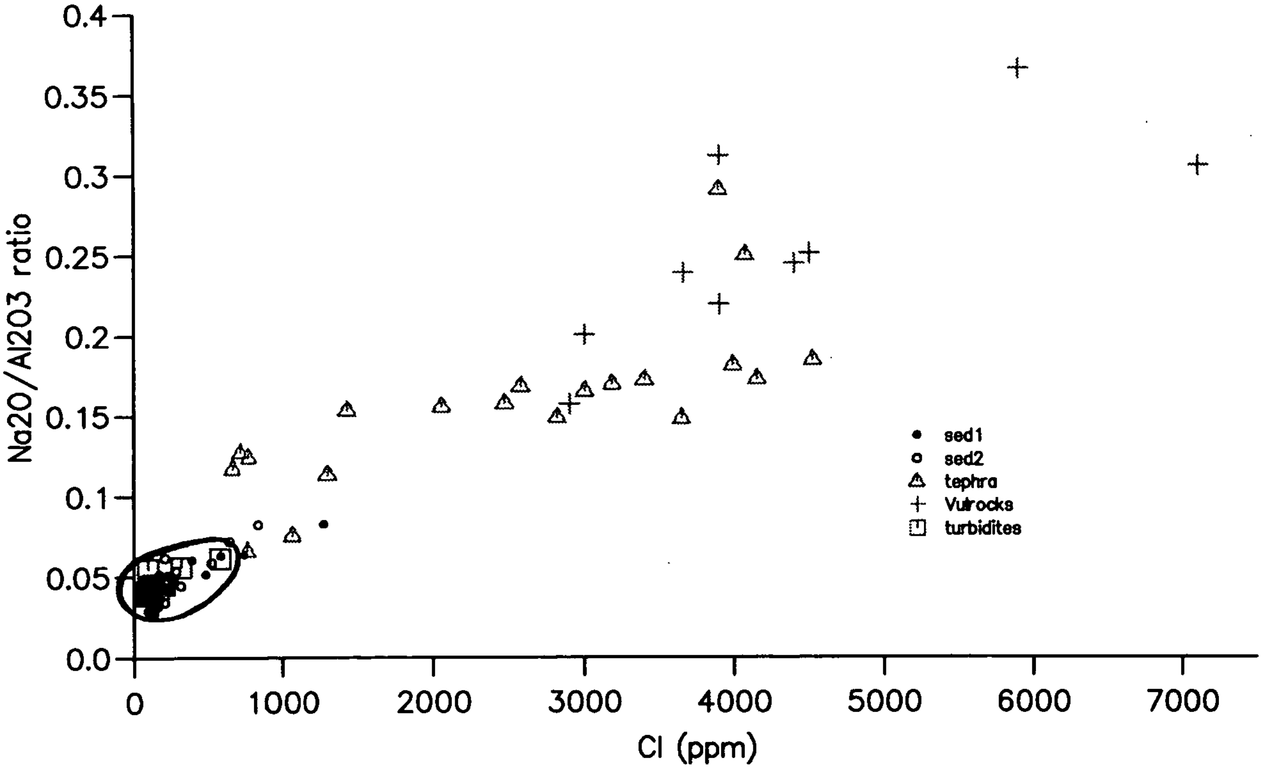


Fig. 4.33. Comparison of turbidite zone samples with other clastic dominated zones around 1500cm (sed1) and 4000cm (sed2) and with major tephra samples and local Vulture rocks (additional data on Vulture rocks from de Fino et. al., 1986)

from Vulture itself. The initial tephra fall might then be correlated with the coarse basal sand layer at 2248cm and the subsequent slump unit and turbidite sequence might reflect the instability caused by an unusually high volume of material being loaded onto the catchment. This, however, is not favoured by geochemical evidence which suggests that the sediments here have much greater affinities with the conventional clastic rich zones at 1500cm and 4000cm depth than with either local unweathered pyroclastics or the trachytic tephra layers (Fig. 4.33.).

The TiO_2 against MgO plot (Fig. 4.33.) shows that the turbiditic sediments are clearly distinct from the group of trachytic tephra layers which contain much lower Ti concentrations. In terms of Mg and Ti, the turbidites show considerable overlap with the Vulture igneous rock group. Together both these groups are more Mg-rich than the normal clastic rich sediment fields. This plot suggests that the turbidites are genetically more likely to be related to a Vulture source than to an external trachytic source. The lower plot (Fig. 4.33.) considers elements that are more sensitive to weathering. In this diagram, both the trachytic tephra layers and the primary Vulture pyroclastics are seen to have high contents of Cl and Na. However, the turbidite group (including the basal sand layer) is clearly distinct from these and associates very closely with normal clastic rich sediment groups. This suggests that the turbidite sediments were subjected to a significant period of subaerial weathering before being deposited and **did not** result from a contemporary pyroclastic input. It is thought that their slightly higher Cl, Na_2O/Al_2O_3 and MgO values in comparison with the normal sediment groups reflect a lower degree of weathering that the material may have experienced. An obvious explanation for this would be if the turbidites had been derived from deep erosion of the local soil system.

The possible mechanisms for increased erosion that might lead to this deposition are thought to include earthquake activity and intense rainfall. It is perhaps unlikely that rainfall alone could cause what appears to be a unique and catastrophic event in the sedimentary record. The Basilicata region is known to be seismically active as evidenced by the major earthquake in 1980 (Chap. 2). It is possible that a large earthquake or tectonic movement could have disturbed the Monticchio catchment allowing initially a large package of crater material to be deposited in the lake. This might include the basal sand **and** overlying slump unit in one depositional event. It is not certain whether the slump unit merely reflects a major and chaotic movement of material into the sediment accumulation zone or whether it has also been disrupted by subsequent liquefaction. Sims (1975) found that seismic disturbances could be recorded in lakes by their effects on surface sediment layers causing liquefaction to take place. Additional quantities of material may have been dumped in unstable littoral or

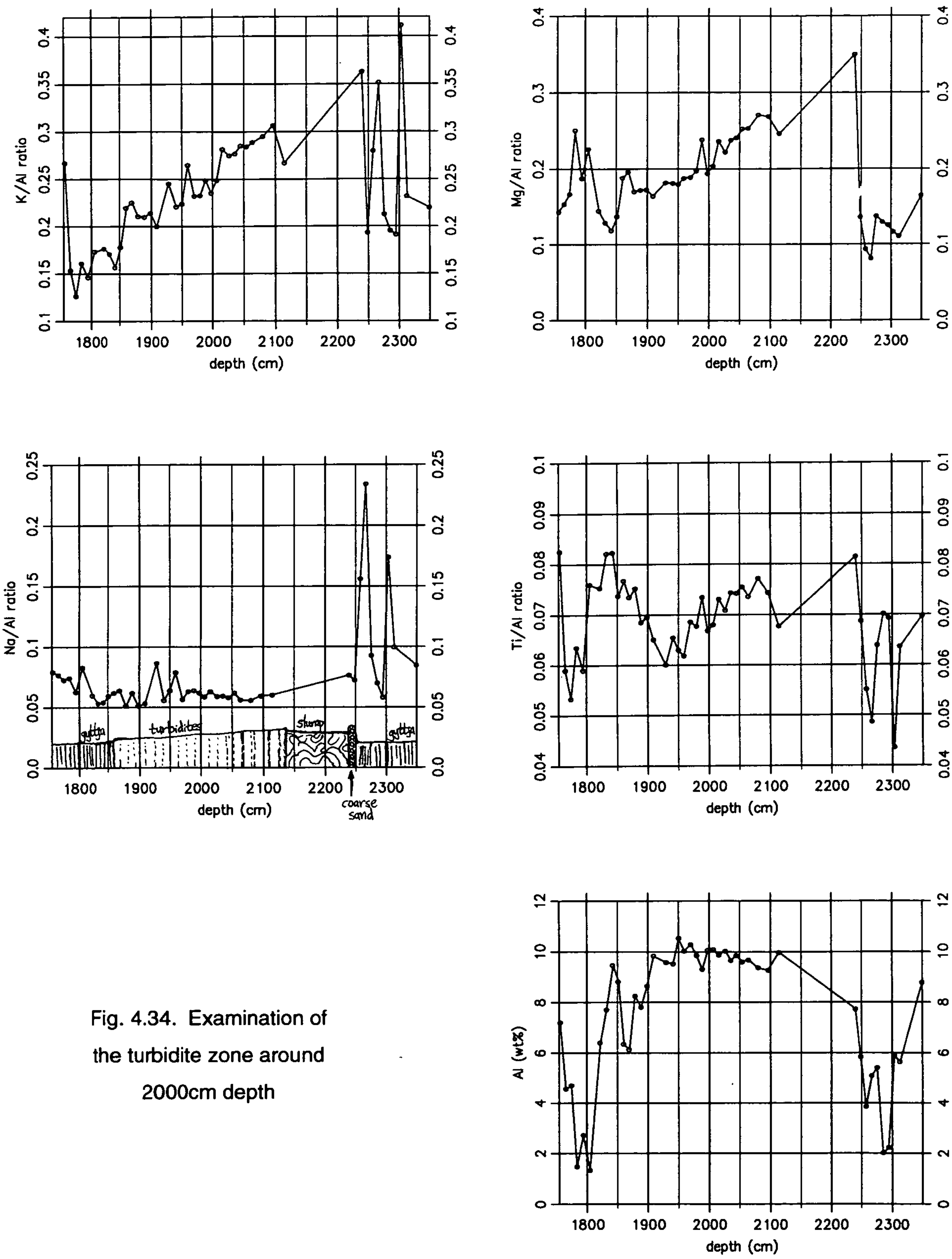


Fig. 4.34. Examination of the turbidite zone around 2000cm depth

nearshore positions by the main disturbance event and these sediments may have later been triggered into turbidity flows by periodic increased rainfall or subsequent earth tremors. Gradually the amount of unstable material available for removal would have diminished and the depositional processes would turn back towards normal suspension settling and accumulation of fine laminae.

Another possibility is that the sediments might record a secondary phreatomagmatic type eruption occurring in what is now the deep pit zone of the lake (Chap. 2). This could have ejected large volumes of bedrock and older sedimentary material and caused an unstable accumulation of debris in the catchment. If this is the case, it may be possible to date this volcanological event quite precisely from a future sediment chronology being established. The validity of this process will require more fieldwork to be tested.

The basic sedimentological division of the turbidite zone is compared with geochemical parameters in Fig. 4.34. It can be seen that the basal coarse sand is not associated with elevated Na/Al or K/Al ratios as would be expected *if* it had been deposited as a primary tephra fall. The ensuing turbidite sequence shows a progressive decrease in Mg/Al, K/Al and Ti/Al ratios thought to reflect decreased contributions of illite-muscovite and pyroxene. This trend is believed to reflect a progressive return to sedimentation dominated by limited surface soil material.

CHAPTER 4c

AUTHIGENIC COMPONENTS OF THE SEDIMENTS

Introduction

This chapter examines both strictly diagenetic components formed within the sediments and endogenic precipitates that are believed to have formed within the lake waters (e.g. calcite). Visual and XRD examination of the Monticchio profile reveals the presence of a number of diagenetic phases, including calcite, siderite, iron sulphides and vivianite. These minerals often occur in distinct and exclusive zones of concentration, but in some instances several phases coexist on a millimetre scale. Some of these minerals occur in narrow and discrete laminae which are believed to reflect rapid formation in a non-steady state environment of deposition. Other products may have developed over longer time scales following sediment burial.

The elemental constituents of these phases are largely derived from the catchment rocks (Engstrom and Wright, 1984). The catchment is believed to represent the fundamental influence both through regulating the level of organic matter deposited in the lake system and as a direct supplier of reactive metals and anions. Secondary effects associated with the internal dynamics of the lake will tend to influence the way in which these components become fixed as authigenic minerals.

Many of the elements used to examine the authigenic features are also present to some degree in the terrigenous clastic fraction. For example, Fe shows pronounced elevations and spikes representative of diagenetic enrichments that are superimposed on a background which probably reflects the relative content of mineral detritus (Fig. 4.35.). This background has a similar shape to the profile for a strict clastic indicator such as Al (Fig. 4.35). In this chapter use of normalisations and ratios to Al will be made in order to remove the effects of changing clastic content. In some elements this is unnecessary since their clastic contribution is negligible and the effects of diagenesis are sufficiently clear from a basic concentration profile.

CALCITE

Calcite was initially identified from thin section examination (B. Zolitschka, unpubl. work) to be present between 1500 and 2300cm depth. The presence of calcite is indicated geochemically through the concentration of inorganic (carbonate) carbon and the concentration of excess Ca (i.e. Ca above that contained in the aluminosilicate fraction). This parameter was estimated from the XRF data by a normative calculation:

$$\text{excess Ca} = \text{Ca} - 0.2 * \text{Al}$$

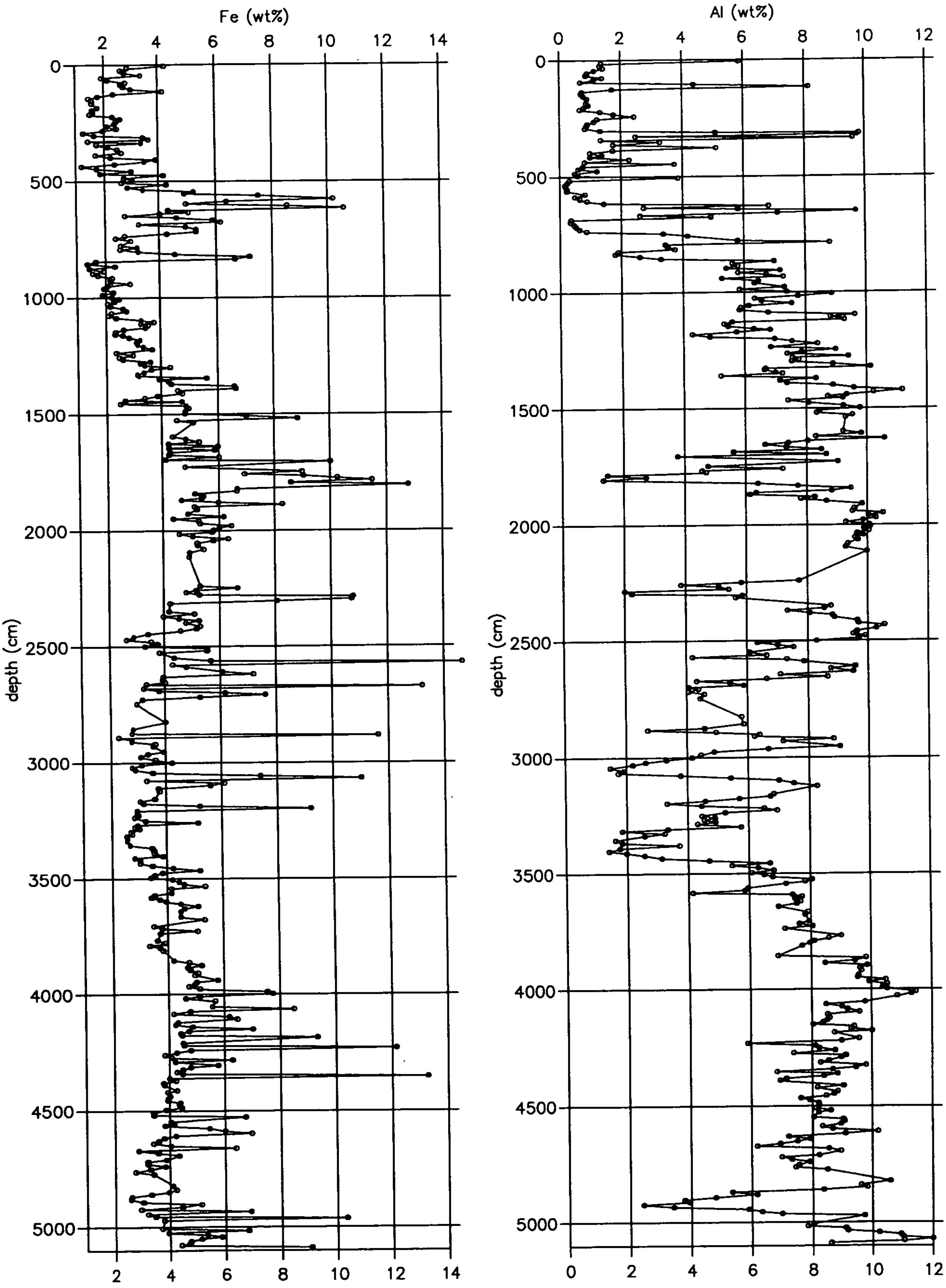


Fig. 4.35. Total Fe and Al content compared

The value of 0.2 was taken as a typical Ca/Al ratio for mudrocks (Turekian and Wedepohl, 1961). Although this may be an inaccurate indicator for low levels of excess Ca, it is thought to provide a reasonable guide where calcite concentration reaches higher levels.

In Fig. 4.36. it can be seen that significant enrichments occur in excess Ca and inorganic carbon between 1500 and 2300cm. Calcite has also been identified by XRD in the top 40cm of the core and in a few other locations, some of which are connected with tephra layers. These areas are also characterised by elevations in excess Ca and inorganic carbon (eg. at 25cm and at 3040cm depth), but of a lower magnitude than the main zone of calcite occurrence. It can be seen from Fig 4.36. that most of the sample points above 2300cm containing significant inorganic carbon are matched by corresponding increases in excess Ca which suggests the presence of calcite. On the other hand, a few spikes above 2300cm depth and the majority of positive zones below 2300cm do not correspond to excess Ca peaks. These other zones are dominated by siderite and will be discussed in the next section.

The principal zone of calcite occurrence is shown in more detail in Fig. 4.37. This plot also includes $\delta^{13}C$ and $\delta^{18}O$ values determined on selected bulk calcite samples using a sequential acid attack (see Appendix 1). The highest calcite concentrations appear to lie between 1700 and 1900cm depth where 3wt% inorganic carbon and 10wt% excess Ca are reached. This is roughly equivalent to around 25wt% $CaCO_3$ in the sediments. This area is interrupted by two minima at 1750 and 1830cm depth where concentrations decrease to near zero. Outside the 1700 to 1900cm zone, 1wt% inorganic carbon is more typical (reflecting <10wt% $CaCO_3$).

There appears to be some relationship between the presence of calcite and the clastic sedimentation discussed in Chap 4b. The first sharp increase in excess Ca and inorganic carbon coincides with the base of the mineral-rich turbidite sequence where a coarse sand and slump unit occur. The following sequence of turbidites is characterised by consistent inorganic carbon values between 0.5 and 1.0wt%. Inorganic carbon (calcite) begins to rise to higher levels above 1950cm which is coincident with the decline in turbidite deposition and a return to 'normal' finely laminated sediments. The laminated sediments throughout the next three metres are typified by high calcite concentrations, but calcite decreases significantly around 1640cm depth. Above this, relatively low calcite concentrations are found with occasional peaks of <1wt% inorganic carbon.

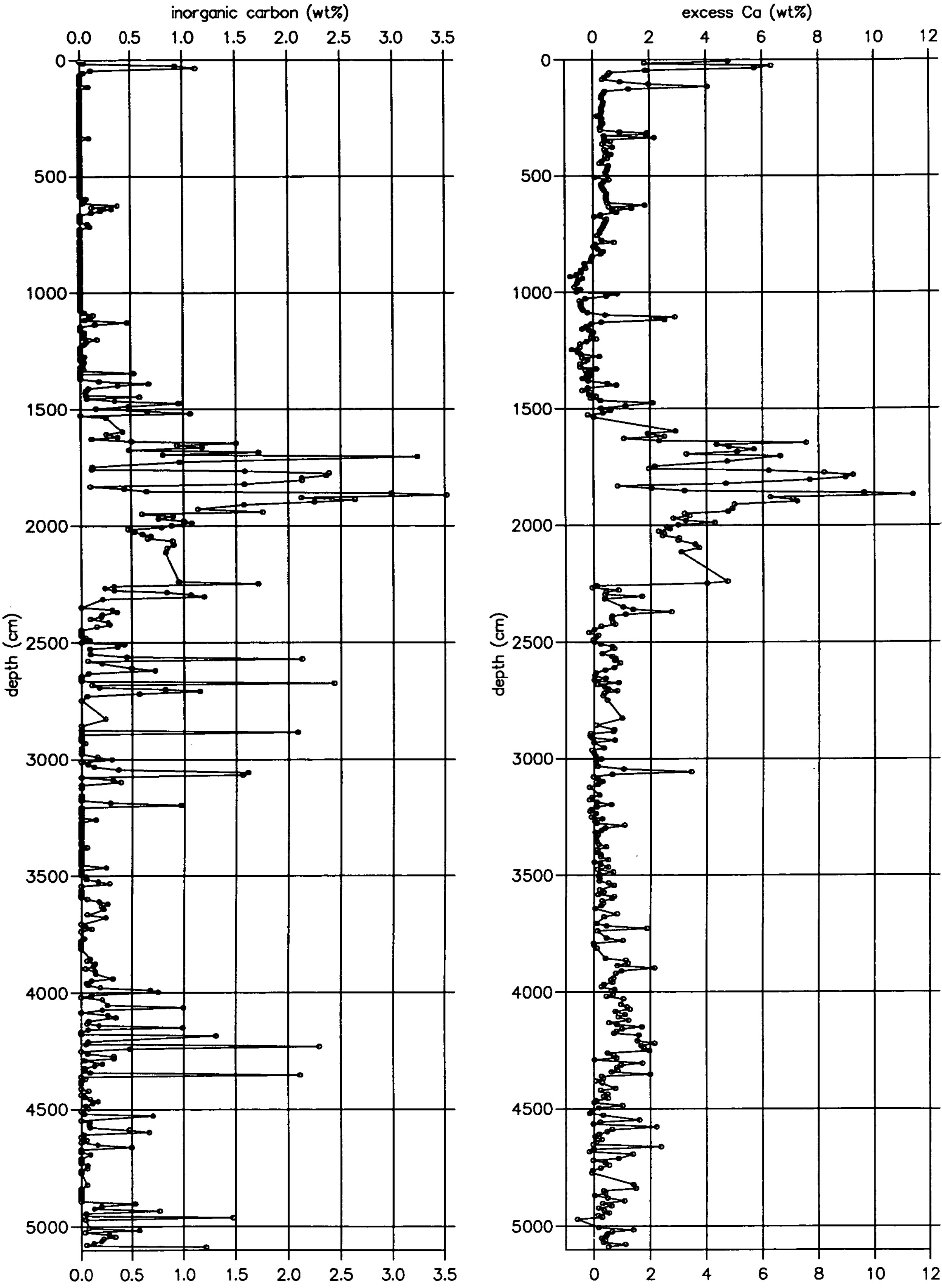
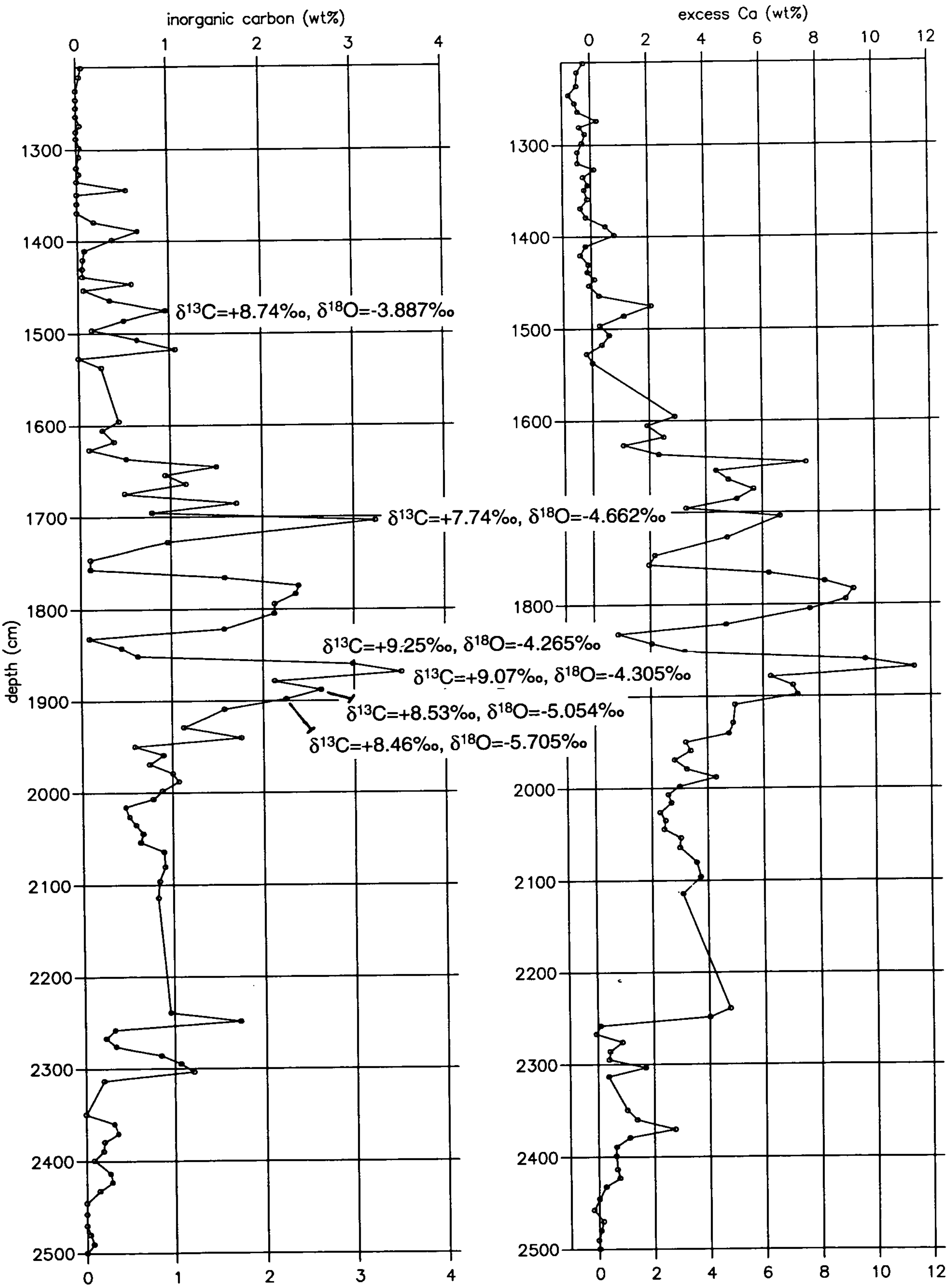


Fig. 4.36. Inorganic carbon and excess Ca



$\delta^{13}C$=+8.74‰, $\delta^{18}O$=-3.887‰

$\delta^{13}C$=+7.74‰, $\delta^{18}O$=-4.662‰

$\delta^{13}C$=+9.25‰, $\delta^{18}O$=-4.265‰

$\delta^{13}C$=+9.07‰, $\delta^{18}O$=-4.305‰

$\delta^{13}C$=+8.53‰, $\delta^{18}O$=-5.054‰

$\delta^{13}C$=+8.46‰, $\delta^{18}O$=-5.705‰

Fig. 4.37. Inorganic carbon and excess Ca for the zone between 1300 and 2500cm ($\delta^{13}C$ and $\delta^{18}O$ values are shown beside selected samples analysed)

Sketches from thin sections prepared for varve analysis (e.g. Fig. 4.38.) show two main forms of calcite to be present throughout this zone: 1) irregular shaped lumps included within actual turbidite layers and presumed to be of detrital origin, and 2) subhedral calcite rhombs occurring in discrete laminae (i.e. solid layers). These layers of calcite crystals may be up to 0.5mm thick and occur **both** between successive turbidite layers in the lower section **and** within the laminated muds above. It is believed that they represent primary inorganic precipitation within the lake (B. Zolitschka, unpubl. work).

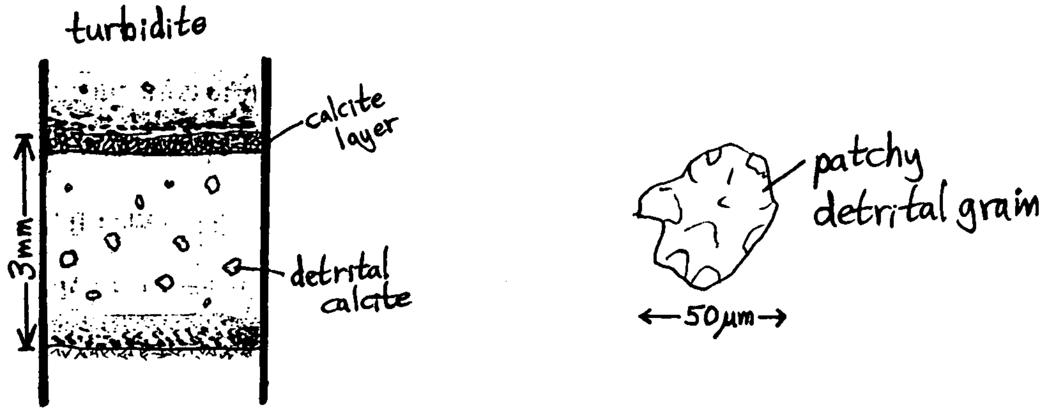


Fig. 4.38. Typical occurrences of calcite.

Ostracods are also found in small quantities between 1450 and 1800cm (Wansard, unpubl. work), but outside this area no evidence for them is preserved. Ostracods reach a maximum in abundance between 1650 and 1735cm which corresponds to the last zone of high calcite concentration, but they are virtually absent in the earlier calcite maxima of 1800 and 1900cm depth.

The low amounts of calcite present in other parts of the core have not been examined in detail, but this calcite is probably typified by thin layers of subhedral crystals/microspar. In some cases dispersed siderite is also present, underlying the calcite level (B. Zolitschka, unpubl. work).

Discussion and interpretation

Reviews (Kelts and Hsü, 1978; Dean and Fouch, 1983) have generally considered lacustrine calcite to be of four possible origins: 1) detrital, 2) biogenic, 3) primary inorganic precipitate, and 4) diagenetic. Primary inorganic precipitation is the most common mode of occurrence for many lake settings, in contrast to the skeletal (i.e. biogenic) dominated sediments of the marine realm. From the above observations, the Monticchio sediments show evidence for at least three of these calcite origins.

The detrital grains of calcite found within turbidite layers are presumed to have either been transported from littoral areas of the lake or to have been eroded from the terrestrial catchment environment. It has been noted by Fiore et. al. (1992) that calcite "pervades" the Vulture volcaniclastic sequence in the form of veins and layers. This calcite is believed to be of secondary origin precipitated from circulating solutions of "deep origin". It is possible that the increased erosional disturbance associated with the onset of turbidite deposition caused calcite present in deeper layers of the weathering profile to be transported to the lake sediments intact or with partial dissolution. Alternatively, an increase in carbonate alkalinity by leaching of newly exposed pyroclastic layers at this time could promote the precipitation of calcite in the littoral zone (perhaps by macrophytes such as Chara). These carbonate crusts or intraclasts could subsequently be broken up and redeposited onto the lake shelf by turbidity currents.

The layers of calcite rhombs probably formed as inorganic precipitates in the surface lake waters and settled to the lake floor. This could represent a secondary response to the increase in alkalinity or carbonate saturation brought about by leaching or dissolution of the new calcitic catchment supply. The two principal mechanisms for inducing calcite precipitation are enhanced algal productivity and temperature increase (Kelts and Hsü, 1978). Both these processes involve the removal of carbon dioxide from the surface waters and tend to be most effective in summer, which is when calcite typically forms. For example, Kelts and Hsü (1978) found that peak formation of calcite occurred between June and August in Lake Zurich, and evidence for this was preserved in the varved sediment sequence. The calcite layers present at Monticchio probably developed during summer also. It is possible that in the early stage (2100 to 1900cm), dominated by turbidites and organic-poor sediments, temperature increase played the dominant role in precipitation. Perhaps the individual turbidite layers were deposited during an autumn or winter season of heavy rainfall and the overlying calcite layer accumulated during the following summer. As organic productivity increased (above 1900cm) it is likely that photosynthetic CO_2 uptake played a greater role in carbonate formation.

Once precipitated, the preservation of calcite depends on the balance between further precipitation and dissolution in the depositional environment. Calcite may dissolve in the hypolimnion/monimolimnion if large amounts of respired CO_2 have decreased the pH balance of the waters. Once buried in the sediment, further stages of dissolution may take place (with possible diagenetic replacement) or the calcite may be permanently preserved. Although the calcite layers in the Monticchio sediments are thought to represent primary precipitates, it is not totally certain that they did not experience dissolution and replacement by a later mineral phase during their post depositional history.

The presence of ostracods provides evidence for biogenic calcite formation in Monticchio. Ostracods suggest oxygenated conditions in the benthic regions of the lake. However, it is not known whether the ostracods present developed in situ or were transported from more littoral regions. More important is likely to be the improved supply of Ca at this time which enabled ostracods to develop and calcify sufficiently so as not to be dissolved after death. Their absence from other parts of the record suggests that Ca in the waters was generally in low abundance for much of the lake's history. In gross terms the ostracods probably represent a minor contribution to the calcium carbonate present.

The minor amounts of calcite present in other parts of the core may sometimes be related to potential alkalinity increases induced by tephra inputs into the system, such as at 630cm depth. Again, calcite formation probably occurred in summer by primary inorganic precipitation and this may have persisted for a short period following the tephra event. In other calcitic areas where there is no tephra association, the formation probably relects change in the evaporative balance of the lake favouring limited carbonate precipitation. The top 50cm of the Monticchio record may reflect an interval when the lake level was artificially lowered (Chap. 2). This may have increased the concentration of alkaline cations or the HCO_3^-/CO_2 balance allowing calcite to form. At other times calcite may have formed in the surface waters, but later suffered complete dissolution, and thus did not survive burial below the upper few decimetres of the sediment pile.

Isotopic evidence

The factors influencing the isotopic composition of primary and diagenetic carbonates have recently been reviewed by Talbot and Kelts (1990) and Talbot (1990). The stable carbon and oxygen values measured on the Monticchio calcites (relative to the PDB standard) range from 7.738 to 9.254‰ and from -5.705 to -3.887‰ respectively. In the discussion of stable isotopic trends it is assumed that Lago Grande di Monticchio represents a closed basin. At present this is correct since the lake is not drained by any outlets, although in the past the lake *may* have at times drained westwards into a valley (Chap. 2).

In a closed basin it is thought that local effects outweigh direct variations caused by change in global climate since the long residence time of the waters in such lakes permits substantial isotopic evolution to occur (Talbot and Kelts, 1990). In other words, changes in global temperature (which affects the isotopic composition of rainwater and the equilibrium carbonate fractionation factor) are secondary to changes in the local evaporative regime of an individual hydrological system. This seriously prohibits the reconstruction of a climatic index comparable to the marine oxygen isotope curve. However, information may be derived concerning the local evaporative balance or organic carbon cycle *if* the catchment hydrology has remained constant.

The $\delta^{18}O$ values of **primary** inorganic calcite depend mainly on the lake water $\delta^{18}O$ values and to a much lesser extent on the temperaure of carbonate precipitation (Talbot, 1990). Lake water $\delta^{18}O$ composition is influenced by both the composition of the inflow supplies (direct rainfall, surface water and groundwater) and by the evaporative balance. Over long periods of time it is possible for closed lakes to develop high $\delta^{18}O$ values, particularly under a pronounced evaporative regime. The $\delta^{18}O$ of **diagenetic** calcite also is influenced by the same factors. It is assumed here that the porewaters in shallow early diagenetic environments are approximately equal to those of the overlying lake waters.

The $\delta^{13}C$ values of **primary** inorganic calcite are influenced by the dissolved inorganic carbon (DIC) composition in the upper water column. This in turn is influenced by a range of factors including the water residence time, lake productivity, inflow composition and the degree of isotopic exchange with the atmospheric CO_2 reservoir. Talbot and Kelts (1990) considered that the first of these factors was the most significant in the case of their African lakes studied. They suggested that preferential outgassing of ^{12}C-rich carbon dioxide from the lake waters over long periods of time would cause the waters to evolve towards progressively higher $\delta^{13}C$ values. This was seen through the covariance of $\delta^{13}C$ and $\delta^{18}O$ values for individual closed basins when suites of primary inorganic carbonates from a particular setting were analysed. In these settings, high $\delta^{13}C$ and $\delta^{18}O$ values were attributed to periods of evaporative enrichment, which had caused both preferential $H_2{}^{16}O$ removal and $^{12}CO_2$ degassing. Other authors have considered the photosynthetic removal of isotopically light CO_2 from the upper waters to be the main influence on carbonate isotopic composition (McKenzie, 1985; Botz et. al., 1988).

Diagenetic calcites may differ from primary inorganic calcites in their $\delta^{13}C$ values, which principally reflect the microbial processes dominant during the early diagenesis of organic matter (Talbot and Kelts, 1990; Irwin et. al., 1977). Processes such as methanogenesis and

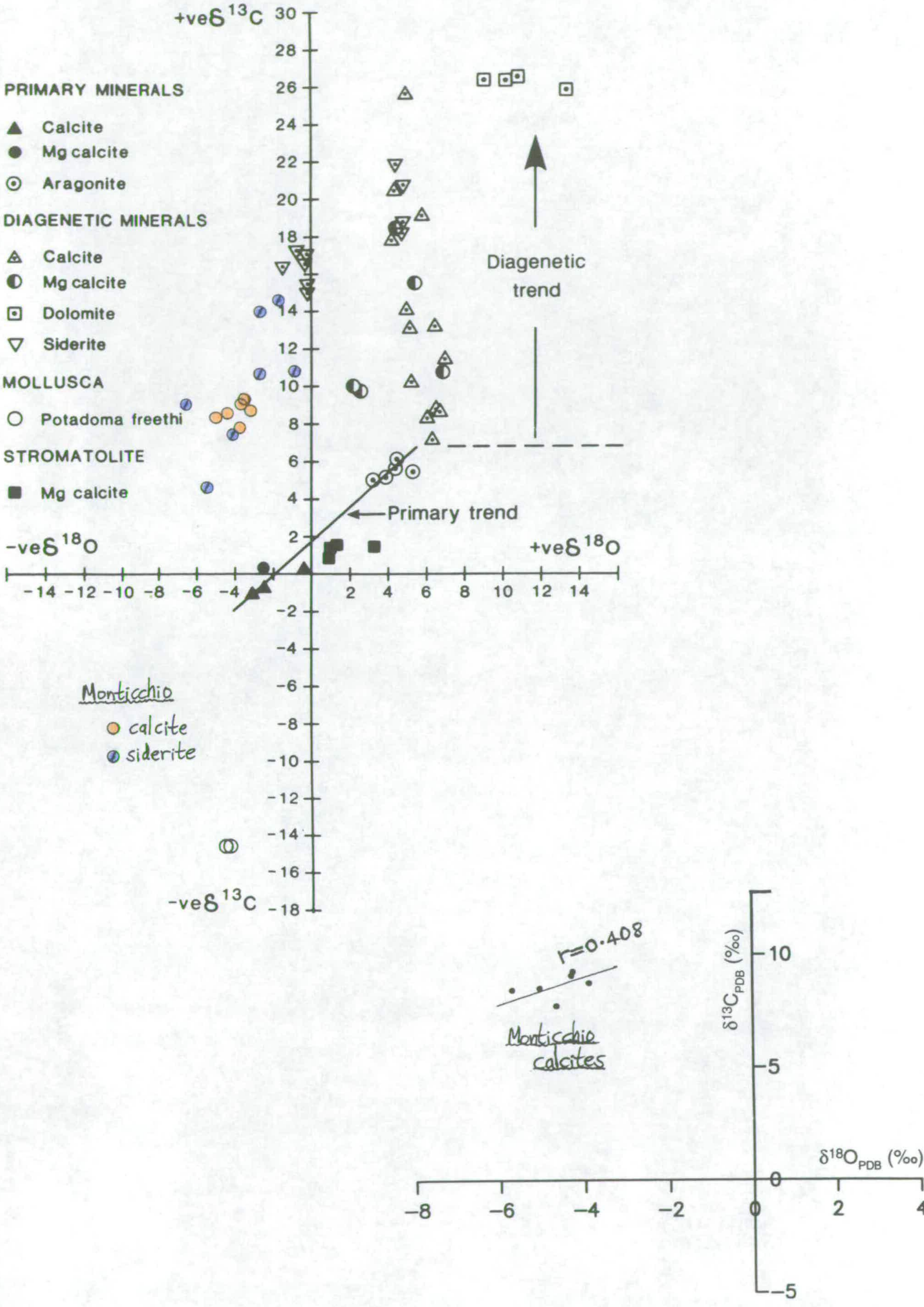


Fig. 4.39. δ13C and δ18O values for Monticchio samples compared with published values for primary and diagenetic carbonates from Lake Bosumtwi (after Talbot and Kelts, 1990)

sulphate reduction can lead to much higher (Talbot and Kelts, 1986) or lower $\delta^{13}C$ values than those produced in primary precipitates, although the $\delta^{18}O$ values will remain much the same. The $\delta^{13}C$ and $\delta^{18}O$ values of diagenetic carbonates do not follow a covariant trend like those of primary precipitates (Talbot and Kelts, 1990). Instead, $\delta^{13}C$ values are often highly dispersed and commonly lie outside the -5‰ to +5‰ range.

Interpretation

The $\delta^{13}C$ and $\delta^{18}O$ values of the calcite samples from Monticchio have been plotted on the same axes as primary and diagenetic carbonates from Lake Bosumtwi for comparison (Fig. 4.39.). The Monticchio $\delta^{18}O$ values show a range of 2‰ which is modest in comparison to certain other studies (Talbot and Kelts, 1990). For Lake Bosumtwi, which experienced dramatic lake level fluctuations, the $\delta^{18}O$ values vary by over 10‰. It is assumed that the changes in $\delta^{18}O$ mainly reflect the evaporative balance and hence the ratio of incoming rainfall to evaporative losses. From the trend observed in $\delta^{18}O$ values (Fig. 4.37.) it would appear that the lake level or precipitation/evaporation balance may have decreased between 1898 and 1475cm depth. This is suggested by the upwards increase in $\delta^{18}O$ from -5.705‰ to -3.887‰. It is possible that the earlier turbidite deposition took place under conditions of higher rainfall and lake level, and that an upwards decrease in rainfall is connected with a decline in turbiditic transportation processes. $\delta^{18}O$ values which lie in the positive field appear to be common in arid or strongly evaporitic settings such as tropical Africa, although latitude and altitude exert additional influences in all cases. The absence of positive $\delta^{18}O$ values in Monticchio and the modest 2‰ variation suggest that any changes in water balance or lake level have not been dramatic over this period. Indeed, there is no other evidence to suggest severe lake level drops elsewhere in the Monticchio record.

The original aim of the isotopic carbonate study was to examine the $\delta^{13}C$ values and compare/contrast these with the $\delta^{13}C$ values of the organic matter. However, results have revealed the possibility of reconstructing past precipitation/evaporation changes and this may be worth pursuing in future work. Further examination might be carried out in particular detail on the zone between 2300 and 1500cm, although it could not be extended to all parts of the record due to the absence of carbonates.

In the interpretation of the $\delta^{13}C$ values it is essential to distinguish between a primary or diagenetic origin for the carbonates. As discussed from morphological evidence, it is believed that the calcite layers represent primary precipitates, but the possibility of replacement of a primary precursor calcite by a diagenetic phase cannot be entirely eliminated.

Assuming a primary origin, the $\delta^{13}C$ values are expected to reflect the $\delta^{13}C$ composition of the DIC in the upper lake waters. The measured values of +7.738 to +9.254‰ are significantly higher than any of the values compiled in a review by Talbot and Kelts (1990). These authors did not find primary carbonate $\delta^{13}C$ values higher than +5‰. Assuming the Monticchio calcites to represent primary precipitates, they display to my knowledge some of the highest recorded $\delta^{13}C$ values in the literature. If the isotopic values are examined on a scatter plot of $\delta^{13}C$ against $\delta^{18}O$ (Fig. 4.39.) the calcite samples appear relatively clustered. This is in contrast to the diagenetic carbonates from Lake Bosumtwi shown on the same axes. It also contrasts with isotopic values for siderite samples (of probable diagenetic origin) from Monticchio which appear to be highly scattered. Talbot and Kelts (1990) observed primary carbonates to be relatively clustered and to show a significant covariance between $\delta^{13}C$ and $\delta^{18}O$ values ($r>0.7$). The six calcite samples measured from Monticchio show a positive correlation of 0.4 (Fig. 4.39.), although this would be better clarified by including a larger number of samples. In general the above evidence favours a primary carbonate origin more than a diagenetic origin.

The high $\delta^{13}C$ values in primary calcites are unlikely to reflect just the evolution of the Monticchio lake waters. This would require intense $^{12}CO_2$ degassing and would be associated with a highly evolved evaporitic trend. The $\delta^{18}O$ enrichments previously described do not support this idea of intense evaporative evolution. It is perhaps more likely that high surface productivity could account for the removal of large fractions of ^{12}C-rich DIC immediately prior to calcite precipitation. This could cause isotopically heavy calcites to form during the mid and late summer season. Such an effect requires extremely limited equilibrium exchange between the lake waters and the atmospheric carbon dioxide reservoir (Schindler, 1975). This may be a reflection of the lake's morphology (e.g. its relatively small surface area). The viability of this hypothesis might be tested by carrying out present day measurements of CO_2 levels and $\delta^{13}C$ values in the DIC pool, both in summer and at other times of the year.

If diagenetic replacement has taken place, it would be most likely that the diagenetic calcite incorporated carbon from a ^{13}C-enriched methanogenic source (Talbot and Kelts, 1990; Bahrig, 1989). Talbot and Kelts (1986) found diagenetic carbonates with $\delta^{13}C$ values as high as +27‰ to be related to pronounced methane formation in the porewaters of Lake Bosumtwi. Both acetate fermentation and CO_2 reduction processes were thought to be participant in this diagenetic environment. Other diagenetic processes such as aerobic oxidation or sulphate reduction would be expected to impart an isotopically light signal from the organic matter to the carbonates and give typically negative $\delta^{13}C$ values. Therefore, the isotopically heavy composition of the Monticchio calcites would suggest the dominance of methanogenesis in the post-depositional environment. This is somewhat contradicted by the evidence for pyrite and high sulphur enrichments (discussed later in this chapter) which suggest that significant sulphate reduction may occur in the sediment zone or in the water column. It would be necessary for this sulphate to become rapidly consumed in the uppermost sediment zone and to be replaced by methanogenesis below to account for the observed $\delta^{13}C$ values. If this was the case, it could be that primary calcite layers survived intact through the sulphate reducing zone and then suffered dissolution on entering the zone of methane production (perhaps due to increased CO_2 levels lowering pH), but were soon after replaced by a new calcium carbonate phase incorporating CO_2 by-products of methane formation. This precipitation might be favoured by a subsequent increase in alkalinity brought about by either microbial CO_2 reduction or the concomitant reduction of Fe and Mn oxides. However, there is no positive evidence of sediment displacement, pore filling, disturbance by nodule growth etc. to suggest that diagenetic formation actually occurred.

It is worth remembering that the samples measured for stable isotopic values represent bulk calcite contents and thus both layered and detrital calcite are included. In general, the layered carbonate phase is likely to represent the largest component. The isotope values presented reflect an average for this mixture while the individual phases may be isotopically different. In a study of the Vulture pyroclastic sequences, Fiore et al. (1992) found $\delta^{13}C$ values of -3.514 to -0.490‰ in calcite material. If such isotopic signatures survived into the sediment record, as the detrital grains, they would have lowered the bulk isotopic values shown, implying that the carbonate layers may have even higher $\delta^{13}C$ values. However, this original calcite may well have dissolved and reformed within the lake environment. Whatever process occurred, it is clear that the lake system has profoundly altered the isotopic composition of any calcite derived from the catchment pyroclastic sequence. It might be possible to further investigate this by extracting individual detrital fragments and material from calcite layers for separate analysis.

SIDERITE

Siderite ($FeCO_3$) was largely unrecognised in the literature on modern lake sediments until the late 1970's (Jones and Bowser, 1978; Anthony, 1977). It was, however, known to be a reasonably common diagenetic phase in ancient lake settings (Fritz et. al., 1971). More recently siderite has been increasingly noticed in modern lakes, most commonly as an early diagenetic mineral although occasionally as an endogenic precipitate in anoxic bottom waters (Bernard and Symonds, 1989). This appreciation of siderite probably reflects both an increase in the type of lakes studied and improvements in analytical and investigation techniques.

In Lago Grande di Monticchio siderite has been identified from preliminary thin section and XRD studies to be widespread over major sections of the profile, particularly during the glacial period(s). Siderite is indicated geochemically by the concentration of inorganic carbon **in connection with** peaks in excess Fe. It is known that complete solid solution exists between siderite and rhodochrosite $MnCO_3$ (Deer et. al., 1985). The likely presence of 'Manganoan siderite' from XRD diffraction trace matches and the high Mn/Fe ratios in certain siderite zones suggest that considerable Mn substitution may be occurring over some periods.

The profiles for inorganic carbon and excess Fe are shown together in Fig. 4.40. The excess Fe parameter is estimated from XRF data by a normative calculation:

$$\text{excess Fe} = \text{Fe} - 0.4 * \text{Al}$$

As with excess Ca, this is thought to provide a good indicator of major siderite and *other* diagenetic iron enrichments, but to be innaccurate at low levels of Fe enrichment.

The upper 10 metres of the profile is thought to be essentially devoid of siderite. Siderite has not been seen in thin section preparations (B. Zolitschka, pers. comm.) or in XRD investigations. This area contains very little inorganic carbon (Fig. 4.40.), but does show noticeable enrichments in excess Fe. It is thought that the minor inorganic carbon peaks present are related to calcite (discussed in the last section) and that the excess Fe maxima (e.g. at 600 and 825cm depth) are attributable to vivianite and iron sulphide associations rather than iron carbonate. This will be described further in the next two sections.

The first occurrence of siderite (identified by XRD) is at around 1120cm depth and from here downwards the mineral is present in greater or lesser amounts for much of the remaining record.

Siderite content increases somewhat from 1120cm towards a first maximum between 1680 and 1880cm depth (Fig. 4.40.). This zone also contains some excess Fe in the form of sulphides. During the preceding turbidite zone between 1900 and 2250cm depth siderite appears to be absent. Carbonate mineralogy in this zone is dominated by calcite. Siderite reappears below 2250cm depth and is found both in minor background concentrations and

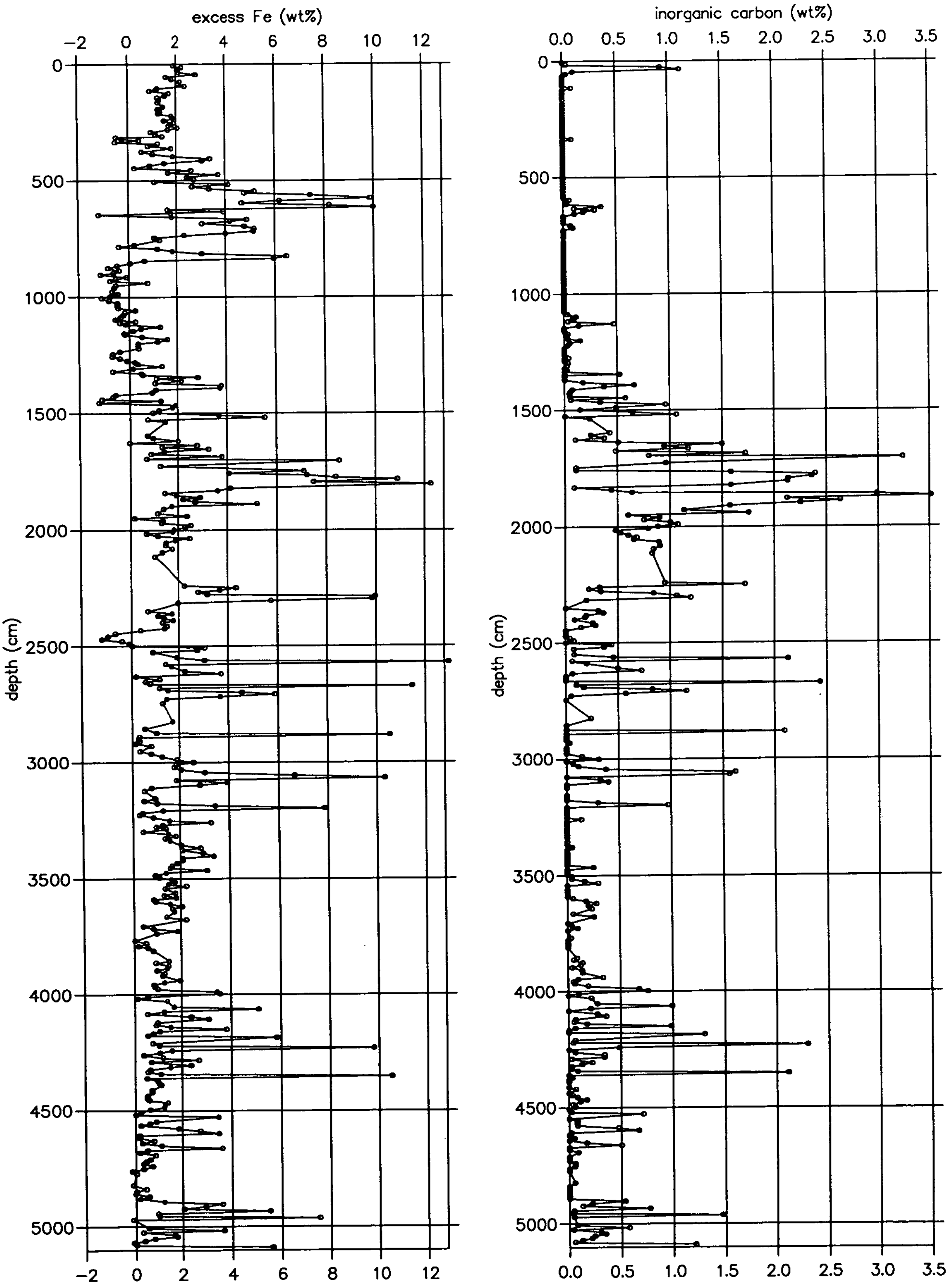


Fig. 4.40. Excess Fe and inorganic carbon

local zones of major enrichment. Areas containing up to 2.5wt% inorganic carbon and 12wt% excess Fe occur. This represents approximately 25wt% siderite content in the most enriched samples. Notable zones of high siderite occur between 2500 and 3200cm and between 3950 and 4370cm. The biogenic silica dominated sediments between 3200 and 3450cm depth are one of the few areas devoid of siderite in the lower profile. This is the interglacial or interstadial period where relative concentrations of clastic mineral material reach a minimum (Chap. 4b). Below 3450cm siderite returns and appears to be reasonably common except for a low around 4700 to 4880cm. It reaches moderate or high values during the interglacial/interstadial period at 4900cm and in the glacial zone below.

Thin section observations

Preliminary examination of the siderite in thin section preparations suggests two main forms: 1) dispersed individual crystals or small granules (<5µm in size), and 2) thin dark horizons (<100µm thick) rich in micritic siderite material and sometimes adjacent to calcite layers (B. Zolitschka, unpubl. work). Sediments containing the diffuse siderite generally have a cloudy yellowish appearance under the microscope.

Mn enrichments

The geochemical indicators for siderite are plotted in more detail in Figs. 4.41. and 4.42. in order to examine the relationship between siderite occurrence and high Mn concentrations. Between 1680 and 1880cm, Mn concentrations are consistently around 1.0wt% and occasionally as high as 3.8wt%. These are extremely high values for a typical mudrock (Turekian and Wedepohl, 1961) and must reflect diagenetic enrichment. The blue shading helps indicate that the Mn peaks are correlated with high inorganic carbon and to some degree with high excess Fe (Fig. 4.41.). It seems possible that up to 25wt% or more manganese carbonate could be substituting in a solid solution with siderite. This situation is complicated by the fact that some excess Fe resides in pyrite and some inorganic carbon is hosted by calcite in this zone. However, it seems most likely that the Mn is principally associated with iron carbonate. This is supported by the XRD evidence suggesting that manganoan siderite is a more likely carbonate phase than pure siderite in these sediments. Further examination by microprobe would provide clearer quantitative information on this association.

In lower parts of the core (Fig. 4.42.) siderite peaks are also associated with *some* Mn enrichment (examples are illustrated by blue shading), but to much lower levels than in the 1680 to 1880cm zone. XRD mineralogy on samples from these areas primarily identified pure siderite as the likely carbonate phase.

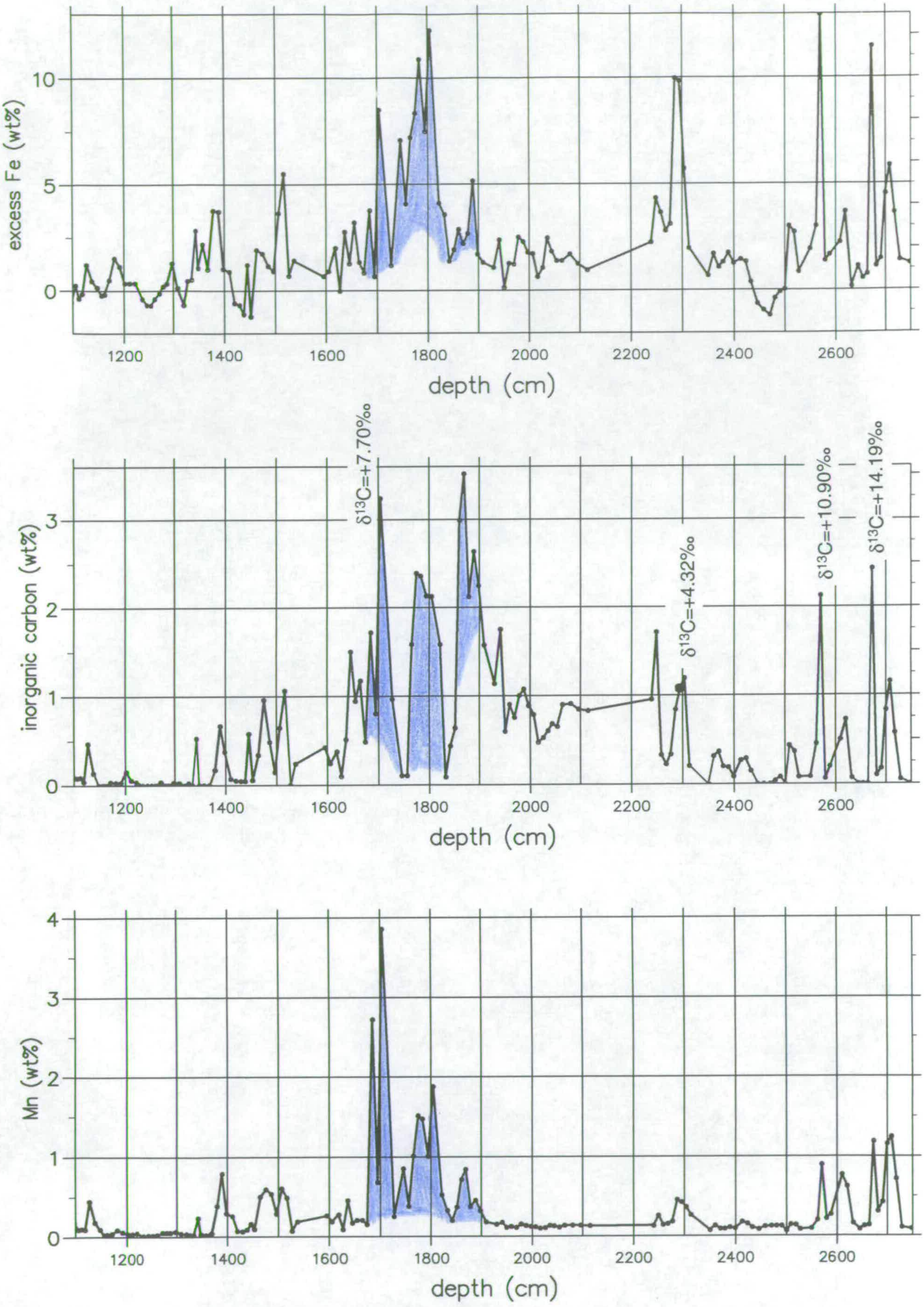


Fig. 4.41. Excess Fe, inorganic carbon and Mn between 1100 and 2750cm depth

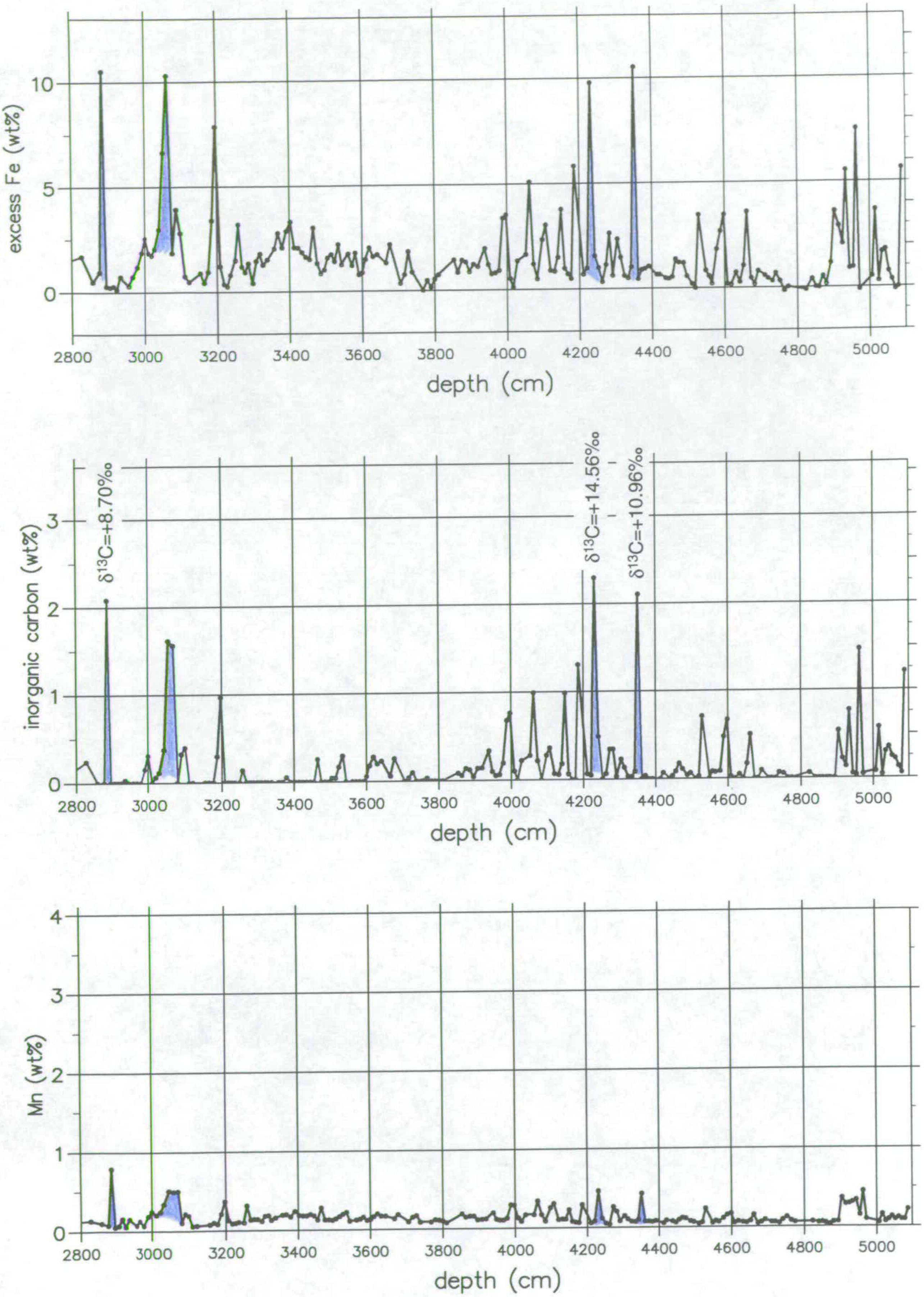


Fig. 4.42. Excess Fe, inorganic carbon and Mn between 2800 and 5100cm depth

Stable isotope observations

Siderite $\delta^{13}C$ values determined on a small number of samples are shown in Figs. 4.41. and 4.42. beside the relevant sample points. The $\delta^{13}C$ values vary between +4.32 and +14.56‰. This represents a relatively broad range (10‰), although all the values lie within the isotopically positive domain. Only seven samples were measured and these come from widely separated areas of the core. This makes comparison of stratigraphic relationships between values difficult and therefore the isotopic data will only be used to make general inferences about carbon sources utilised in carbonate formation. Also, the trends in $\delta^{18}O$ values will not be discussed.

Discussion

The conditions required for siderite formation have been described by many authors (Bahrig, 1989; Postma, 1981; Berner, 1971). The main requirements are:

1) low Eh: reducing conditions are necessary for the thermodynamic stabilisation of siderite and for mobilisation of a sufficient amount of Fe^{2+}
2) low dissolved sulphur (SO_4^{2-}, H_2S) concentrations: if sulphur is available iron sulphides will be formed in preference to siderite
3) high pCO_2 and/or increased alkalinity
4) high Fe/Ca ratios (>0.05) in the formation waters

Increase in the availability of the main ingredients (i.e. Fe and CO_3^{2-}) is one obvious way in which siderite formation might be favoured. In the Monticchio environment it is likely that iron oxyhydroxides in the catchment zone provide the main Fe source. These are predicted to exist in the soil zone as weathering products of the underlying pyroclastic rocks. Primary igneous minerals such as pyroxene which may also contain iron are generally considered to represent a secondary source (Curtis et. al., 1986). They are much less available towards microbial activity in the diagenetic zone and unlikely to mobilise significant Fe^{2+} in comparison with the oxyhydroxide phases. Fe bearing components may be transported to the lake sediments in particulate form by erosion or in solution through leaching processes and possible subsurface water movement. It is possible for an increase in Fe supply to arise either through increased erosional intensity or through increased leaching from a soil horizon. The latter may take place if the soil humus content develops and the soil environment changes to a more reducing one (Engstrom and Wright, 1984). Bicarbonate is most likely to be supplied from the decomposition of organic matter either in the lake waters or in the buried sediments. Increase in bicarbonate supply could arise through increased microbial degradation (perhaps in response to increased organic deposition). The resultant

pCO_2 increase alone would tend to lower pH and discourage carbonate precipitation. However, accompanying microbial processes such as sulphate reduction or Fe(III) reduction cause alkalinity to increase and offset this trend.

As well as changes in Fe and bicarbonate supply, a change in siderite occurrence could also be related to change in the biochemical conditions within the lake. Siderite formation may be favoured by redox, pH or sedimentation rate changes. Such factors represent a complex interplay between catchment inputs and the internal dynamics of an individual lake.

Most palaeolimnological studies have interpreted siderite as an early diagenetic mineral forming within the upper few centimetres of the sediment column (Truze, 1990; Giresse et. al., 1991). Reconstructions generally describe the reduction of a surface layer of ferric oxyhydroxides (supplied from external sources) which undergoes burial below a redox boundary (e.g. Fig. 4.43.). The subsequent ferrous iron which becomes mobilised and concentrated in porewaters reacts with bicarbonate produced by decay of organic matter in the sediments and precipitates as a carbonate mineral. The process is aided by the attendant increase in alkalinity caused by Fe(III) or sulphate reduction.

Truze (1990) associated the occurrence of siderite with intermediate climatic conditions in Lac du Bouchet. During interstadial periods vegetation cover was reduced enabling high rainfall events to wash iron oxyhydroxides into the lake from the catchment soils. These became reduced within the sediment zone and formed siderite with carbon produced from organic matter decomposition. In contrast, during glacial times soil erosion events also occurred, but sedimentary organic matter may have been too low to generate sufficient bicarbonate and so the iron was preserved as a ferruginous layer. During vegetated interglacial periods the catchment slopes were relatively stabilised and Fe supply from detrital inwash may have been too low.

A few studies have interpreted siderite as an endogenic precipitate forming in anoxic lake waters. This is usually connected with conditions of high dissolved Fe^{2+} in monimolimnion waters ('iron meromixis'). Formation occurs when the solubility product of siderite is exceeded either by increase in $[Fe^{2+}]$ or $[HCO_3^-]$. In the case of Lake Nyos siderite precipitation was assumed to have occurred after catastrophic CO_2 degassing from the monimolimnion. This caused a sharp rise in alkalinity under conditions in which high concentrations of dissolved iron had built up (Bernard and Symonds, 1989).

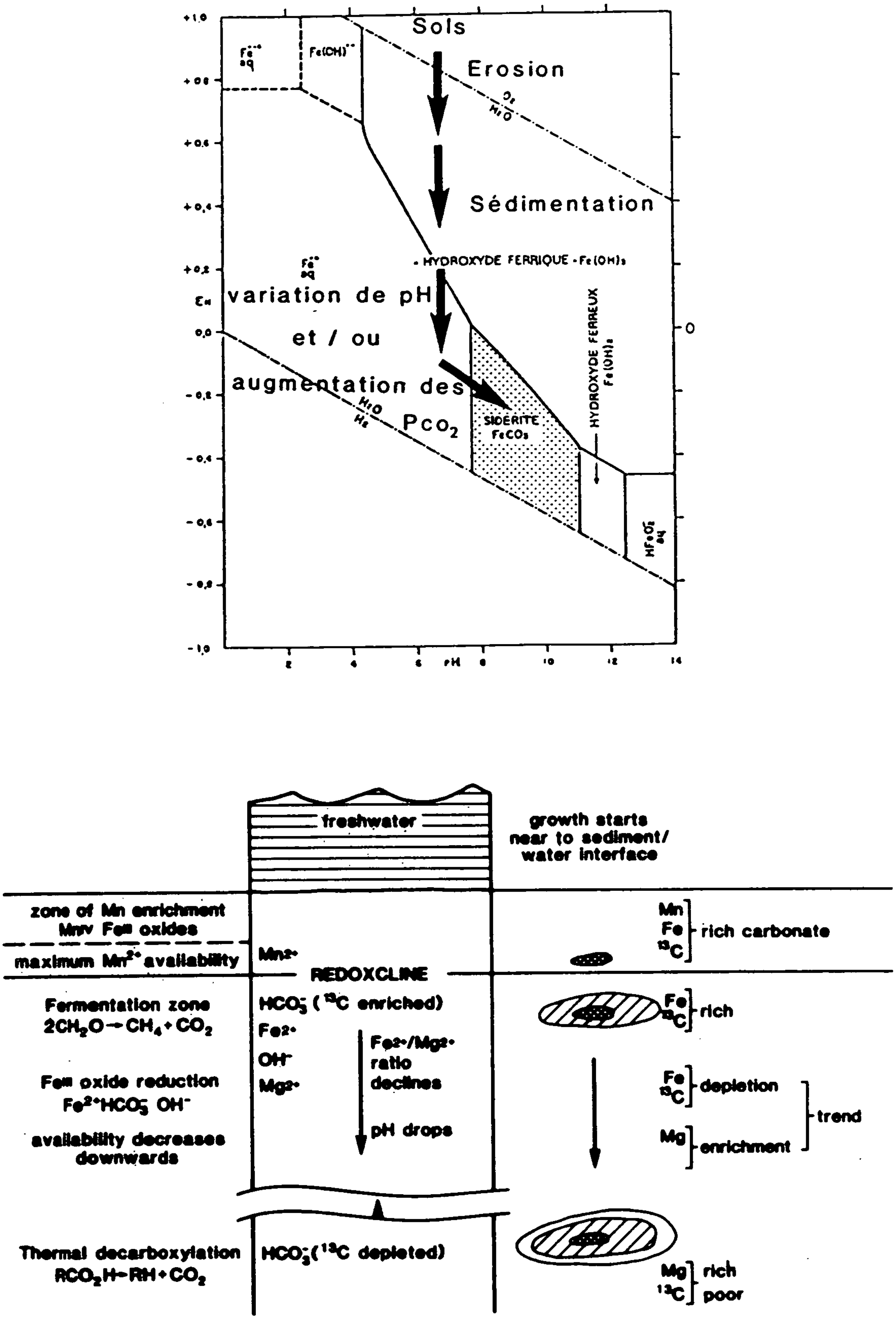


Fig. 4.43. Phase diagram pathway for siderite formation (after Truze, 1990) and model for diagenetic carbonate phases in freshwater sediments (Curtis et. al., 1986)

Since siderite does not form under oxidising conditions it is unlikely that the mineral would reflect the $\delta^{13}C$ value of DIC in the suface oxygenated waters. The $\delta^{13}C$ values of siderite are likely to reflect either the composition of the DIC in a the hypolimnion/monimolimnion environment or the DIC in the sediment porewaters. Under more unusual conditions volcanic CO_2 emissions can contribute to the DIC in these zones (Schoell et. al., 1988). The possibility of this process is suggested by preliminary field observations at Lago Grande di Monticchio (Chap. 2), but requires further investigation to justify in this case. For the moment, the $\delta^{13}C$ values of the siderite will be interpreted in terms of the DIC supplied by organic matter decomposition and the dominant microbial processes involved in this supply. As with the discussion of $\delta^{13}C$ values for diagenetic calcites (last section) the same processes are thought to govern the isotopic composition of siderites (Talbot and Kelts, 1990; Curtis et. al., 1986). The positive $\delta^{13}C$ values of the siderites measured suggest that methanogenesis provides the dominant supply of bicarbonate in this setting. Aerobic oxidation or sulphate reduction dominated bicarbonate supply would lead to characteristically negative isotopic compositions. In oxygenated lakes methanogenesis normally occurs at some depth below the sediment water interface and thus carbonates incorporating methanogenic DIC products would normally be associated with formation after sediment burial (i.e. in the early diagenetic environment). Methanogenesis might take place under anoxic conditions within the actual lake waters, or methanogenic products could diffuse upwards into the overlying lake waters under conditions of stratification (Kelly et. al., 1988; Schoell et. al., 1988). This might enable siderite to form in the lake waters or on the sediment water interface with the incorporation of methanogenic carbon. In the Monticchio sediments, the often dispersed or diffuse-horizon form of the siderite and the presence of significant pyrite in some zones (particularly around 1800cm depth) suggests that formation occurred after burial and that methanogenesis is more significant below the sediment surface.

Most siderites are known to show some degree of Mn substitution. Fe and Mn have very similar ionic radii (0.75Å and 0.80Å respectively) and substitution should be expected. It is thought that Mn substitutes into $FeCO_3$ in preference to the crystal stuctures of either vivianite or iron sulphide (Postma, 1981). Therefore, in the absence of a separate Mn phase, siderite is most likely to be the host in this environment. Most lacustrine sediment studies have found only limited Mn-substitution (<5% $MnCO_3$) in siderites (Bahrig, 1989; Singer and Ehrlich, 1978). This is particularly the case for siderites assumed to have formed under conditions of anoxic stratification (Dickinson, 1988; Bernard and Symonds, 1989).

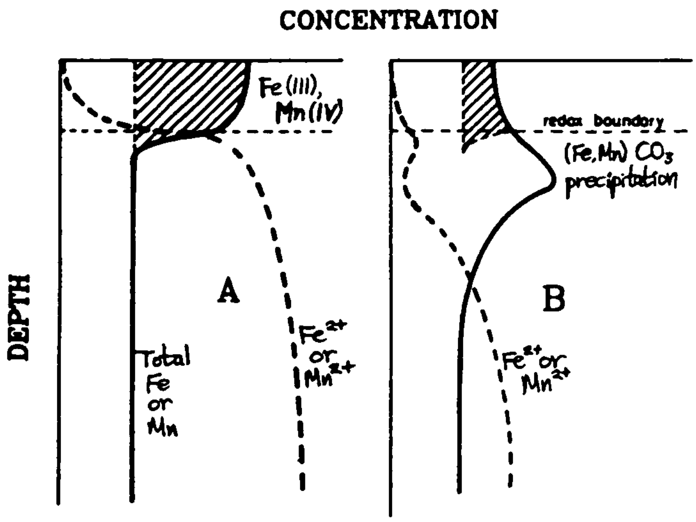
It is generally believed that the enrichment of Mn in sediments requires the presence of an aerobic environment above the sediment zone (Wersin et. al., 1991; Pedersen and Calvert, 1990). This is because particulate bound Mn(IV) is preferentially reduced to Mn(II) as soon as oxygen disappears from the environment and will remain in solution (not precipitating as a solid phase) in oxygen deficient waters. Therefore the presence of Mn enrichments has been taken to imply oxic conditions within the overlying water -conditions which must extend to at least a thin layer of the surface sediments. With an oxic top Fe(III) and Mn(IV) oxyhydroxides are concentrated or precipitated in the surface layer and the loss of Mn^{2+} or Fe^{2+} from the sediments by upward porewater diffusion is impeded. This enables high concentrations of dissolved Mn^{2+} (and Fe^{2+}) to build up in the zone immediately below the oxic surface layer (Fig. 4.44a.). Since Mn(IV) is predicted as the next electron acceptor to be utilised after free oxygen (Kelly et. al., 1988; Froelich et. al., 1979) Mn^{2+} will preferentially accumulate over Fe^{2+} *immediately* below the oxic boundary. In this environment, bicarbonate (or other ligands) can combine with the dissolved Mn and Fe and form a diagenetic precipitate (Fig. 4.44a.). The newly stabilised Mn-rich phase may then survive continued burial into the anoxic zone. Studies of diagenetic minerals classically associate Mn-rich concretions or horizons with early diagenetic formation under oxic bottom waters (Curtis et. al., 1986). This is illustrated in Fig. 4.43.

Interpretation

The presence of siderite over much of the lower part of the Monticchio record indicates that the conditions for siderite formation were appropriate for much of this time period. This probably included the low availability of dissolved sulphur (Postma, 1982), if not in the lake waters then at least rapid consumption of sulphate in the uppermost sediment layers. The high $\delta^{13}C$ values suggest that methanogenesis was the dominant mechanism of organic matter breakdown within the sediment zone where siderite formed. The absence or very low abundances of pyrite in these sediments (B. Zolitschka, unpubl. work) agree with this trend. Both organic matter and iron oxyhydroxides supplied by the catchment soils were in reasonable availability. Occasional siderite enrichments might reflect periodic inwashing of higher quantities of soil material increasing the supply of Fe. This could also provide more associated organic matter of terrestrial origin, thought by some authors to provide favourable substrates for siderite formation (Bahrig, 1989). It is less probable that increased productivity (leading to increased methanogenesis) drove the peaks in siderite as the organic carbon record is essentially low and constant throughout this time.

The absence of siderite in the biogenic rich sediments around 3300cm depth could reflect a reduced supply of catchment eroded Fe due to vegetation rise and soil stabilisation. This might be expected to favour an increase in *leached* Fe due to the soil environment becoming

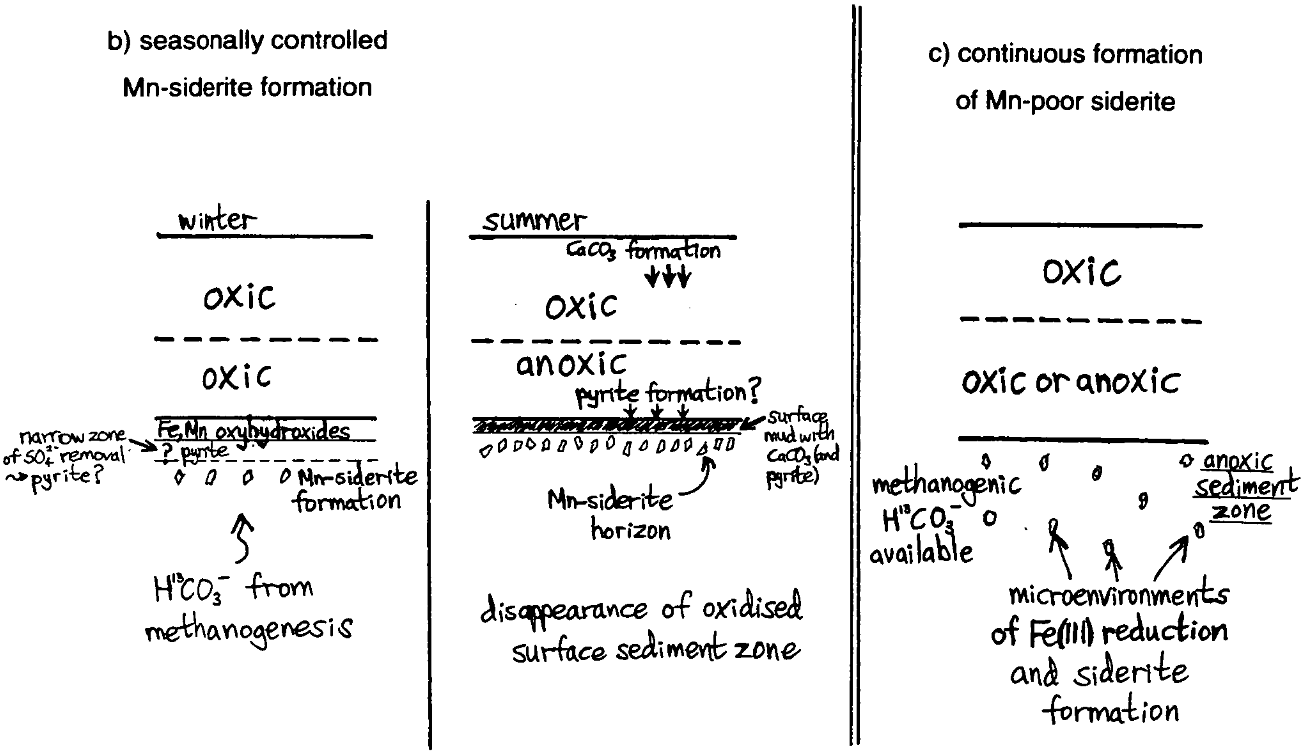
Fig. 4.44. Models for siderite formation



a) Hypothetical distribution of Total Fe or Mn (solid line) and pore water Fe^{2+} or Mn^{2+} (dashed line)

A: burial balanced by upward diffusion of pore water

B: non-steady state development of a siderite forming zone due to presence of HCO_3^- below the oxic-anoxic boundary (modified from Carignan and Tessier, 1988)



b) seasonally controlled Mn-siderite formation

c) continuous formation of Mn-poor siderite more reductive through a build up in surface humus. However, increased Fe supply by leaching does not appear to be the main influence on siderite formation in this case.

The lack of siderite at 2100cm in the turbiditic zone is probably related to decreased Fe^{2+}/Ca^{2+} ratios induced by the external loading of calcite onto the lake system (c.f. Singer and Ehrlich, 1978). This would influence the lake water environment and probably also the early diagenetic environment through downwards diffusion of Ca^{2+} (and possibly also partial dissolution of calcite within the sediments). At the same time, the catchment may have been stripped of soil oxyhydroxides by severe erosion and may have required time to recover from a primary state. Gradually the calcite loading to the system may have been fixed in the sediments and renewed supplies of oxyhydroxides begun through a return to soil development and weathering. This would have promoted the reappearance of siderite above 1900cm.

The siderites between 1880 and 1680cm which show large Mn-enrichments are assumed to have developed under at least periodically oxic lake water conditions. The fact that sub-millimetre horizons of siderite and also pyrite occur in alternation suggests that seasonally related changes in redox conditions may be operating. It is suggested that the lake may have been holomictic during this time. In this situation the lake waters may have undergone circulation in the winter months causing oxygenation of the hypolimnion. This would allow a thin layer of ferric oxyhydroxides and associated Mn(IV) to form on the sediment surface (Anthony, 1977). Immediately below this surface layer high concentrations of Fe^{2+} and Mn^{2+} might develop in the porewaters (Fig. 4.44b.). If methanogenic CO_2 was being produced within the underlying sediments it is possible that the HCO_3^- availability permitted the rapid fixation of a sideritic horizon along this boundary zone (i.e. before the Fe and Mn had time to be recycled upwards). It might be expected that an intervening zone of sulphate reducton would occur between the oxic surface and the methanogenesis dominated sediments below. This would be supported by a diffusive flux of sulphate from the overlying waters. Thus iron sulphide formation might occur immediately prior to siderite precipitation (Fig. 4.44b.). The fact that siderite also exists suggests that the dissolved sulphate was consumed before all the iron had been removed and so further reactions (with HCO_3^-) were possible. Mn^{2+} does not form a stable sulphide phase under normal lake conditions (Wetzel, 1975) and so would not have been incorporated until the carbonate forming stage.

As increased surface productivity supplied organic matter to the hypolimnion during the summer months the surface oxic layer would decay due to oxygen depletion in the bottom waters. It would at the same time become buried by new sediment and move towards the reduced environment. The disappearance of this oxidised layer would be associated with the loss of Mn^{2+} (and Fe^{2+}) from the sediments to the hypolimnion waters (Moss, 1988; Wetzel, 1975) and further precipitation of Mn bearing phases would cease. It is possible that as anoxic conditions developed, organic degradation in the hypolimnion zone continued by sulphate reduction. This might cause H_2S to accumulate in the hypolimnion and precipitate a small quantity of pyrite crystals in the water or at the sediment surface during the summer (Fig. 4.44b.). There could also be a periodic fallout of calcite crystals precipitated in the surface waters, adding another component to the sediment accumulation. These layers would then become preserved in the sediment above the earlier subsurface siderite formation and development of another microsequence commence the following year.

Such processes require narrow boundary zones (<0.25mm) containing sharp chemical gradients to exist (Davison, 1981) and minimal surface disturbance in order to be preserved in the sediment record. The presence of ferrogenic varves in lake sediments (O'Sullivan, 1983 and refs. therein) supports the possibility for seasonal cycles in lake biochemistry being recorded in such ways.

The absence of siderite from the upper 1100cm may reflect a reduced supply of Fe from soil erosion or the increasing productivity of the lake system. The latter may have, through increased P levels, favoured vivianite development in preference to siderite or altered the redox or pH (too acidic?) conditions discouraging the formation of siderite. This may simply reflect the imbalance between large amounts of organic matter in the sediments, but insufficient ferric oxyhydroxides.

Further discussion

It is possible that the seasonally controlled redox mechanism presented to explain the occurrence of Mn-enriched siderites may have a general association with high siderite content and with siderite in the form of concentrated horizons. This mechanism may have prevailed both at 1680 to 1880cm depth and in other parts of the core which display elevated siderite contents. The amount of Mn-enrichment at these times may have varied due to other factors, such as catchment supply. Siderite enrichment periods interpreted in terms of increased inwash of soil detritus may have also benefited from the increased water circulation connected with the rainfall or erosional activity. This may have prolonged the establishment of a surface oxidising layer and sustained rapid siderite formation below. In contrast, the diffuse (<5µm) granular form of siderite may reflect slower continued nucleation and growth in microenvironments below the most active diagenetic zone (Fig. 4.44c.). Micro-environments favourable to siderite formation might arise due to local centres of Fe(III) reduction. It is possible that this more dispersed type of growth continued after early rapid formation of a sideite horizon or it may have represented the only form of siderite formation for some periods. The process might have operated under both oxic and anoxic surface conditions. At the moment more investigation of the thin sections and mineral chemistry is required to test these ideas.

VIVIANITE

Vivianite $Fe_3[PO_4]_2.8H_2O$ has been documented as an early diagenetic mineral in lacustrine sediments where reducing conditions prevail (Nriagu and Dell, 1974; Rosenqvist et. al., 1970; Mackereth, 1966). Interest in its occurrence has been enhanced by the role that iron-phosphorus associations play in regulating nutrient regeneration between sediment and the overlying lake waters (Paalman et. al., 1993; Manning et. al., 1991): a subject of increasing relevance due to the problems of man-made (and natural) eutrophication in lake environments (Moss, 1988).

Observations

The occurrence of vivianite in the Monticchio sediment record was immediately apparent from visual examination following extrusion of the core sections. The blue partially oxidised form of the mineral was observed between 560 and 710cm depth in the organic rich Holocene section and around 4930cm depth in a deeper part of the record. Deep blue patches (<5mm in size) were seen sparingly distributed on the exposed core surfaces. Interpretation of these masses as concretions of primary origin requires care: it has been found in some studies that vivianite may crystallise in voids after sediment cores have been collected (Giresse et. al., 1991).

Vivianite is indicated in the geochemical profiles by high P enrichments which correlate with high excess Fe values (Fig. 4.45.). The outstanding feature of the P record is the pronounced peak between 500 and 750cm depth during the early Holocene. In this zone total P contents of up to 2.5wt% are matched by excess Fe values reaching 10wt% (Fig 4.45.). This trend in the chemical stratigraphy corresponds broadly with the visual observations just described. Above and below this zone P remains at what appears to be a background level. The P profile for the rest of the core is probably dominated by detrital contributions in the form of apatite. This appears to be a prevalent phase in the sediment record (Chap. 4b). P contents for the later Holocene are around 0.1wt% while the higher values for the glacial sections (0.2-0.5wt%) probably reflect increased contents of detrital apatite.

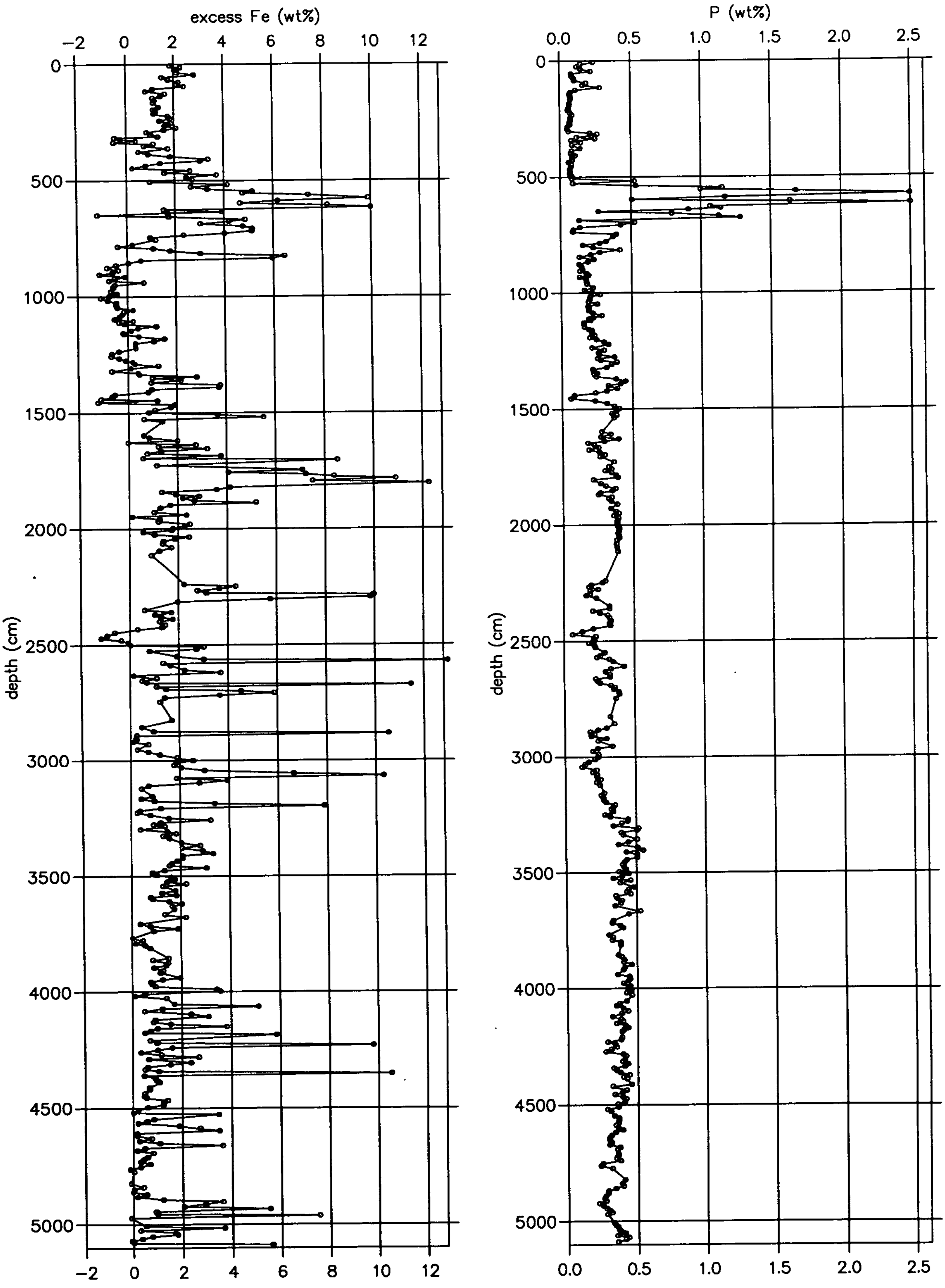


Fig. 4.45. P and excess Fe

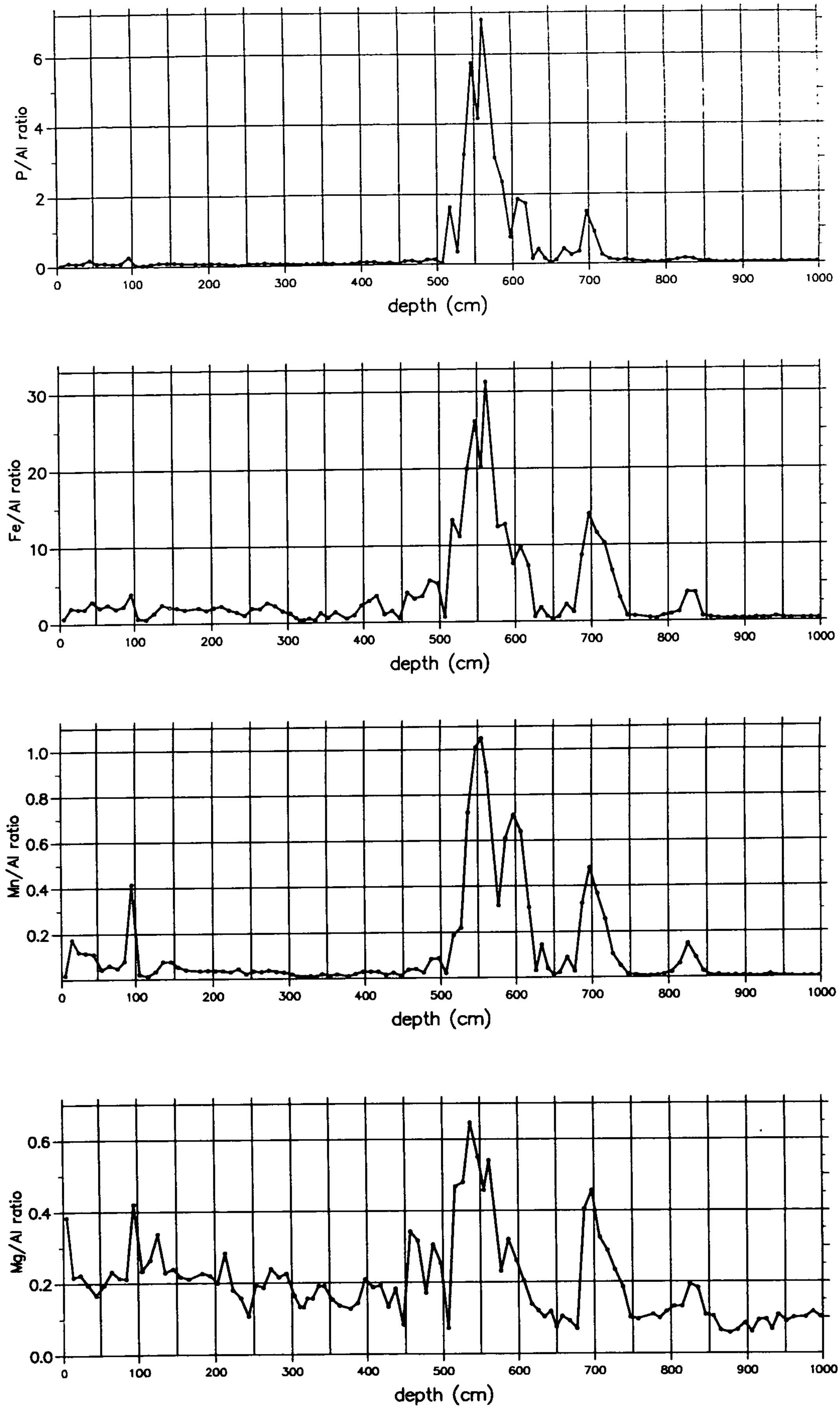


Fig. 4.46. P/Al, Fe/Al, Mn/Al and Mg/Al ratios for the upper 1000cm

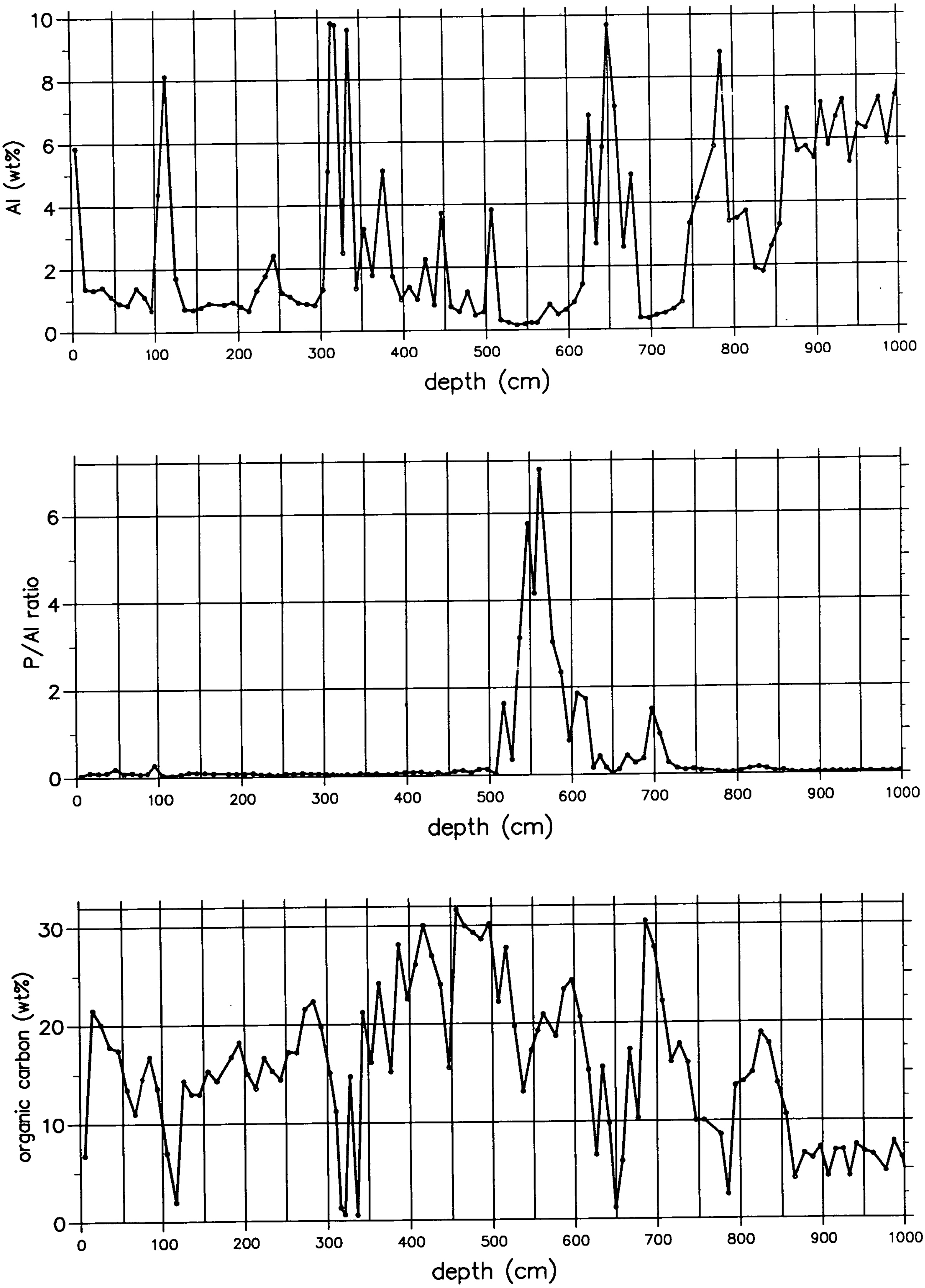


Fig. 4.47. Al, P/Al ratio and organic carbon for the upper 1000cm

The vivianite observed around 4930cm is not highlighted by enhanced P concentrations. It was neither seen in the P/Al profile which might exaggerate the presence of P enriched samples. On the other hand, a slight elevation in P around 3400cm may be associated with the presence of vivianite. It would seem that the two interglacial/interstadial zones of 3400 and 4900cm depth show only weak concentrations of vivianite in comparison with the early Holocene.

The Holocene section is examined in more detail in Figs. 4.46 and 4.47. The profiles shown here represent P, Fe, Mn and Mg as ratios to aluminium. This has been used to remove the variations caused by clastic tephra additions. The P/Al ratio is characterised by a principal peak around 560cm and a secondary maximum around 700cm. A slight maximum also occurs around 825cm depth in what might be a late-glacial interstadial period. Outside these areas the P/Al ratio is at a base level suggesting that only minor amounts of vivianite may be present elsewhere. The Fe/Al ratio shows corresponding trends to the P/Al profile (Fig. 4.46.). Also Mn/Al and Mg/Al ratios show parallels with the P/Al profile suggesting that these elements may be substituting in a vivianite phase. Their relative contribution, however, is greatly exaggerated by using ratios to aluminium. It is thought that <0.1wt% excess Mg and <0.5wt% excess Mn are present in comparison with 10wt% excess Fe during the vivianite maximum. The approximate excess Fe/P ratio here appears to be 4 which is somewhat higher than the predicted Fe/P ratio for vivianite of 2.7. This suggests that some excess iron may be present in the form of iron sulphides and perhaps also unreduced Fe(III) components.

In Fig. 4.47. P/Al, as an indicator of vivianite, is compared with organic carbon and aluminium contents. The P/Al and organic carbon profiles show approximately similar trends (r=0.405) between 1000 and 525cm, with peaks in P/Al corresponding to the highest organic contents. However, above 525cm organic carbon rises to further high contents, but P/Al drops to a base level and remains low for the rest of the Holocene. This suggests a possible relationship between vivianite formation and high organic productivity (or nutrient status) during earlier times, but later on organic-rich accumulation was not accompanied by abundant vivianite.

The Al content is used to examine possible relationships between tephra zones (high Al content) and vivianite concentration. It can be seen that the two main P/Al peaks are separated by a tephra rich zone between 620 and 680cm (Fig. 4.47.). It was wondered whether the deposition of coarse unweathered clastic material into the lake might stimulate subsequent vivianite formation. Although there is an alternation of clastic rich periods and major vivianite occurrence below 500cm there appear to be no vivianite enhancements associated with later tephra zones, such as at 320cm. Thus there does not appear to be a consistent relationship with tephra deposition, and this is supported by the evidence from thin section examination described below.

XRD examination of two samples from 580 and 650cm depth found that the blue mineral analysed most closely matched vivianite or baricite $(Mg,Fe)_3[PO_4]_2.8H_2O$. The possibility of two phosphatic phases being present cannot be ruled out, but the two minerals identified have very similar diffraction spectra (Sameshima et. al., 1985). It is more likely that a single mixed cation phase, such as $(Fe,Mn,Mg)_3[PO_4]_2.nH_2O$, may account for the observed diffraction traces. Pyrite was also identified in these samples suggesting that vivianite formation and sulphate reduction may be occurring in close associaton.

Examination of thin section preparations has shown vivianite to be present "almost all over" the profile (B. Zolitschka, unpubl. work), but usually in small quantities. It is observed to be more abundant around 4920cm and above 1500cm depth, reaching highest concentrations during the early Holocene. The vivianite tends to occur as discrete layers of euhedral to anhedral crystals. These are in the form of both individual tablets or needles (<50µm) and rosette-like aggregates containing many crystals (<100µm). Their occurrence in narrow zones or layers suggests formation during short intervals of time, rather than slow growth of concretionary nature. No direct association is seen between the vivianite crystals and any tephra layers; instead the crystals occur in many locations throughout the gyttja.

Discussion

The conditions for vivianite precipitation are similar to those for siderite, although high PO_4^{3-} concentrations relative to HCO_3^- are required (Postma, 1981). Vivianite may also be favoured by decreased pH. This is illustrated by a phase stablity diagram (Fig. 4.48.). The formation of vivianite may be discussed in terms of Fe and P supply and the conditions favourable to its precipitation in lacustrine environments.

Increased supply of Fe and/or PO_4^{3-} from the catchment would be expected to favour the formation of vivianite. Supply of Fe is probably governed by the same factors as discussed for siderite. That is, input of soil oxyhydroxides from catchment erosion (and perhaps leaching) may provide the major source. Phosphate may be supplied by direct leaching releasing dissolved PO_4^{3-} to the lake or it may be transported bound to soil oxyhydroxides or humic complexes (Engstrom and Wright, 1984). Detrital apatite will also supply particulate P

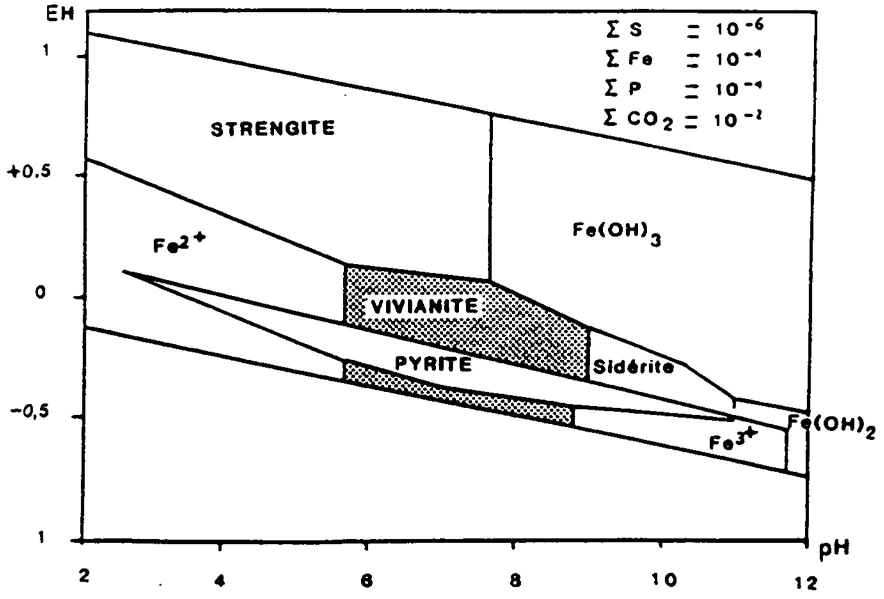


Fig. 4.48. Phase stability field for vivianite (after Truze, 1990)

to the lake sediments, but this is normally unavailable to diagenetic processes (Manning et. al., 1991; Krauskopf, 1967). During the Holocene, stabilisation of the catchment by increased vegetation cover may have reduced the supply of Fe and PO_4^{3-} by erosion and so leaching may have provided the main supply route.

Vivianite formation requires elevated concentrations of Fe and PO_4^{3-} in the sediment pore waters (Nriagu and Dell, 1974). However, dissolved PO_4^{3-} is often found to be rapidly recycled from the sediments to the lake waters by organic decomposition (Gale et. al., 1992). Emerson and Widmer (1978) found in Greifensee that >85% of the PO_4^{3-} released by the mineralisation of organic matter was returned to the overlying lake waters. In such cases it may be difficult for sufficient interstitial concentrations of PO_4^{3-} to build up in order to allow vivianite precipitation.

It is believed that PO_4^{3-} retention in lake sediments is strongly regulated by the presence of Fe (Bortelson and Lee, 1974). In particular iron oxyhydroxides, if present, can efficiently bind large quantities of PO_4^{3-} ions by surface adsorption. This commonly occurs in oxic lake environments where a surface Fe-oxyhydroxide layer exists. This layer will minimise PO_4^{3-} losses from the sediments by upward diffusion and may be associated with a pore water build up of Fe^{2+} and PO_4^{3-} in the reducing boundary zone immediately below (Carignan and Flett, 1981). Under conditions of high PO_4^{3-} concentration vivianite is thought to form, perhaps acting as a buffer which regulates P levels in the interstitial waters (Nriagu and Dell, 1974).

It is normally considered that vivianite precipitates from Fe^{2+} and PO_4^{3-} in solution, although some authors have argued for the possibility of solid state conversion (reduction) of a surface Fe(III)-PO_4^{3-} layer to vivianite (Nembrini et. al., 1988).

It is possible that in a seasonally anoxic lake, periods of overturn and oxygenation are associated with the development of a ferric layer in the surface sediments preventing PO_4^{3-} removal. Subsurface vivianite formation might occur during or immediately after these periods. When periods of stagnation and anoxia follow the Fe(III) layer may dissolve allowing ferrous iron and PO_4^{3-} to leave the sediments and occupy the hypolimnion. This trend may be readily reversible on a yearly timescale and might be recorded in the sediments under suitable conditions.

Despite conditions of high pore water supersaturation, vivianite may fail to precipitate or may grow very slowly due to low surface reaction rates (Emerson and Widmer, 1978). Nucleation and crystal growth can be enhanced in organic-poor coarse grained sediments due to their higher porosities (Pedersen, 1979). The tephra sand and silt layers might offer such a substrate in the Holocene sediments, but vivianite is not found to be associated with these zones. Zelibor et. al. (1988) showed that gelatinous media such as lacustrine gyttjas which form under high organic matter deposition are beneficial to vivianite formation. In such media well-formed aggregates of vivianite can rapidly develop and this situation may apply in the case of the organic-rich Holocene sediments.

Interpretation

The occurrence of vivianite appears to be associated with periods of high organic productivity. This contrasts with siderite occurrences which seem to provide the dominant form of Fe enrichment during glacial and interstadial periods. Vivianite is found mainly during the early Holocene, although minor elevations probably exist during the 3400 and 4900cm interglacial/interstadial periods. Sedimentation at these times was probably influenced by high nutrient supply from the catchment (Chap. 4a) and resulted in high depositional rates of organic matter. Vivianite may have been favoured by the increased PO_4^{3-} fluxes arising from the decomposing sedimented matter. The formation of vivianite may also have been favoured over siderite by the balance between organic matter decay (generating CO_2 and lowering pH) and Fe(III) reduction (generating alkalinity). Much higher levels of organic matter generated acidity in comparison to modest Fe(III) contents available for reduction would be unfavourable to carbonate precipitation (Morse et. al., 1992). However sufficient Fe was available to allow PO_4^{3-} to be retained, probably under at least seasonally oxygenated conditions. This would have enabled vivianite to precipitate just below the sediment surface.

Thus catchment nutrient (PO_4^{3-}) supply ultimately drove vivianite formation and the less organic rich (lower nutrient input) periods of 3400 and 4900cm depth (Chap. 4a) are reflected by lower amounts of vivianite. Dissolved sulphur must have been in low availability during these times or did not diffuse far into the sediment profile if available in the lake waters. The trace quantities of vivianite found in other parts of the core, such as between 1500 and 850cm, may reflect local microenvironments favourable to vivianite formation which did not prove to be extensive. Individual or diffuse occurrences of vivianite may typify these areas (B. Zolitschka, unpubl. work).

The early Holocene Mn-enrichments associated with vivianite suggest the presence of oxic conditions at least seasonally in the lake waters. It was found in Lake Erie that Mn-enriched vivianite occurred below ferromanganese oxide surface sediments (Nriagu and Dell, 1974). The degree of Mn-enrichment is not as high as in the siderites between 1680 and 1880cm depth and this may reflect the more limited solid solution thought to be possible between Fe and Mn phosphates (Postma, 1981). Alternatively, the ratio of Mn to Fe supplied from the catchment may have been lower or the oxygenation conditions in the lake less supportive towards Mn-enrichment. The presence of possibly annual vivianite layers showing Mn-enrichment may be explained in a similar way to the case for siderite (last section). During winter overturn an Fe oxyhydroxide layer may have developed in the surface layer allowing vivianite to form immediately below while conditions of oxygenation prevailed. A narrow zone of sulphide reduction may have existed between the oxic layer and the vivianite precipitating zone below. Alternatively, Fe sulphides may have formed during the subsequent period of stagnation and anoxia. Varve subunits with vivianite-rich horizons have been documented from autumn and winter couplets in a number of lakes (Negendank et. al., 1990; Simola et. al., 1981).

The presence of vivianite in the early post-glacial sediments of the Lake District, but not in later sediments was observed by Mackereth and interpreted as reflecting slow diagenetic growth rates. This was later disputed by Rosenqvist (1970), and many other studies have suggested that vivianite may develop under much shorter time intervals. The presence of vivianite in the early Holocene of Monticchio in what would appear to be seasonal growth horizons suggests that the absence of this mineral from later sediments is not due to the slow rate of formation, but rather the lack of favourable conditions. The most obvious explanations for this seem to be: 1) reduced Fe supply from the catchment, or 2) a change to permanently anoxic conditions preventing sufficient interstitial PO_4^{3-} build up. The fact that Fe (as vivianite) has been fixed to the sediments in high quantity during the early Holocene is clear from the elevated Fe profile. It is therefore necessary to balance the Fe buried to the sediments with new Fe from the catchment for continued vivianite formation (Manning et. al., 1991). However, the change to a catchment dominated by leaching processes may have prohibited the continued supply of significant Fe. It may be the case that Fe is carried into the lake more effectively by soil erosion than by solution, or perhaps the exposed soil layers have become progressively depleted in Fe. Therefore although high phosphorus fluxes still exist from the sediment to the lake there is no agent to retain this migration. On the other hand, if Fe availability had remained the same, but oxygenation of the hypolimnion had decreased, a ferric layer would no longer form on the sediment surface and the bottom waters would hold high concentrations of Fe^{2+} and PO_4^{3-} rather than the sediments. Prolonged anoxicity has implications for other aspects of the sedimentation and evidence for this might be looked for in the presence or absence of benthic microfossils.

SULPHIDE MINERALS AND SULPHUR ASSOCIATIONS

In non-evaporitic lakes sedimentary sulphur tends to be present in the form of Fe sulphide phases and organic-bound sulphur (Rudd et. al., 1986). There has recently been considerable debate as to the relative importance of organic sulphur and iron sulphides as sinks for this element (Carignan and Tessier, 1988 and refs. therein). Conditions of sulphur fixation appear to be significantly different for individual lakes and appear to be particularly dependent upon the availability of reactive iron and the redox regime(s) in the sediments and lake waters. Further geochemical and isotopic studies seem to be necessary before this question is fully resolved.

Observations

A strong black colour was observed in the sediments between 500 and 850cm depth when the core sections were freshly extruded (c.f. Plate 3.). This colouration has often been attributed to the presence of iron monosulphides (Davison et. al., 1985; Jones and Bowser, 1978; Emerson, 1976). It is thought that only a minor amount of sulphide is required to impart a black colour to fine grained sediments (Kelly et. al., 1991). In contrast, other sections of the core such as the glacial periods and the Holocene above 500cm are greyish or brown in colour suggesting that little Fe monosulphide is present. Since being in storage the core sections have lost their black colour and are stained with reddish brown iron oxides. No samples from the Monticchio record were found to produce a pronounced H_2S odour when warmed with acid, although a vague hint of H_2S was provided by some of the sediment samples from the early Holocene. This suggests that Fe monosulphides are only present in minor quantities in the record.

Measurement of sulphur

Sulphur was measured by Carlo Erba® CNS analyser and by XRF on pressed powder discs. Both results profiles show similar trends (Fig 4.49.) although there is considerable doubt as to the accuracy of the Carlo Erba values (see Appendix 1). Therefore the XRF data will be used in the following discussion.

The S profile is shown beside the organic carbon profile in Fig 4.50. There appears to be a good correlation between the two elements (r=0.748). This is considerably higher than the correlation between S and excess Fe (r=0.428). Indeed, if the area between 1000 and 2000cm is excluded the correlation between S and organic carbon increases to r=0.828. These results suggest the possibility of an organic sulphur association in the sediments and this is supported by evidence discussed below. However, between 1000 and 2000cm there is an elevation in the S profile which does not appear to be matched by organic carbon. Sulphur content here reaches a peak of 7wt% around 1800cm depth. It is thought that in this zone the presence of iron sulphides (pyrite) is significant. This is further illustrated by the similarities between total sulphur/organic carbon (S/C_{ORG}) ratio and excess Fe (Fig. 4.52). The correlation between S and excess Fe in this zone is much higher (r=0.838).

In Fig 4.51. the ratios of S/C_{ORG} and C_{ORG}/S are shown. The high values (>0.5) on the S/C_{ORG} profile immediately highlight the zone thought to be influenced pyrite S. In particular, values are elevated between 1150 and 1900cm, but the positive spike at 2250cm is more attributable to the low organic carbon content of this sample. Above 1150cm and below 2300cm S/C_{ORG} values are typically below 0.5. Tephra layers which are very low in organic carbon content, but have modest sulphur contents provide occasional positive spikes to the record. If the inverse C_{ORG}/S ratio is examined it can be seen that none of the samples measured has a value greater than 11. The Holocene and late-glacial period are associated with C_{ORG}/S ratios between 4 and 10, showing considerable fluctuations. In contrast, samples from early parts of the record (below 2250cm depth) are predominantly associated with C_{ORG}/S ratios between 2 and 6. Thus, if these areas are assumed to be dominated by organic sulphur, it would seem that the earlier organic matter zone contains higher S contents than that of the Holocene. Nevertheless, both areas have unusually S-rich compositions.

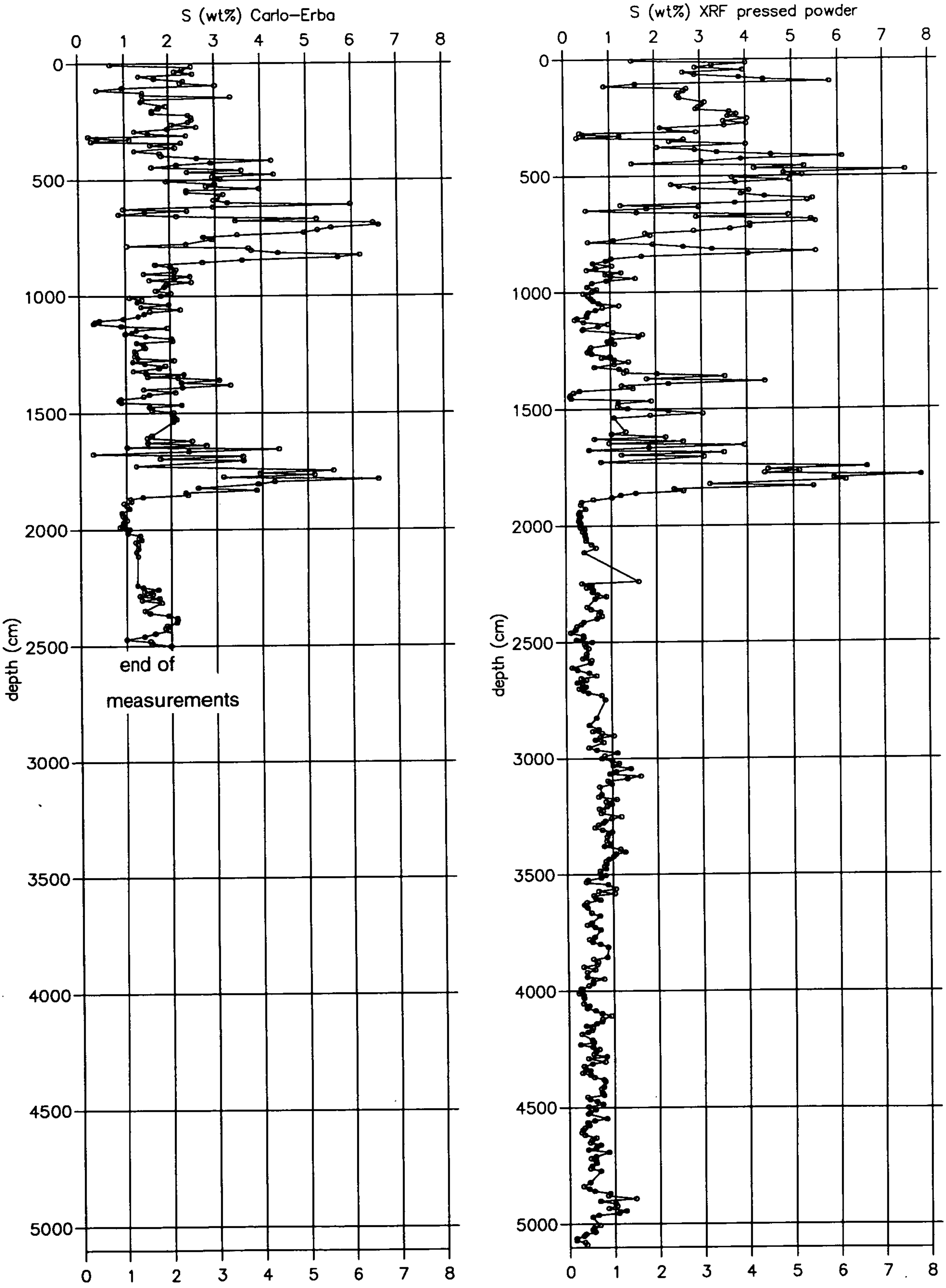


Fig. 4.49. Comparison of total sulphur measurements by Carlo Erba® elemental analyser and by XRF on pressed powder discs

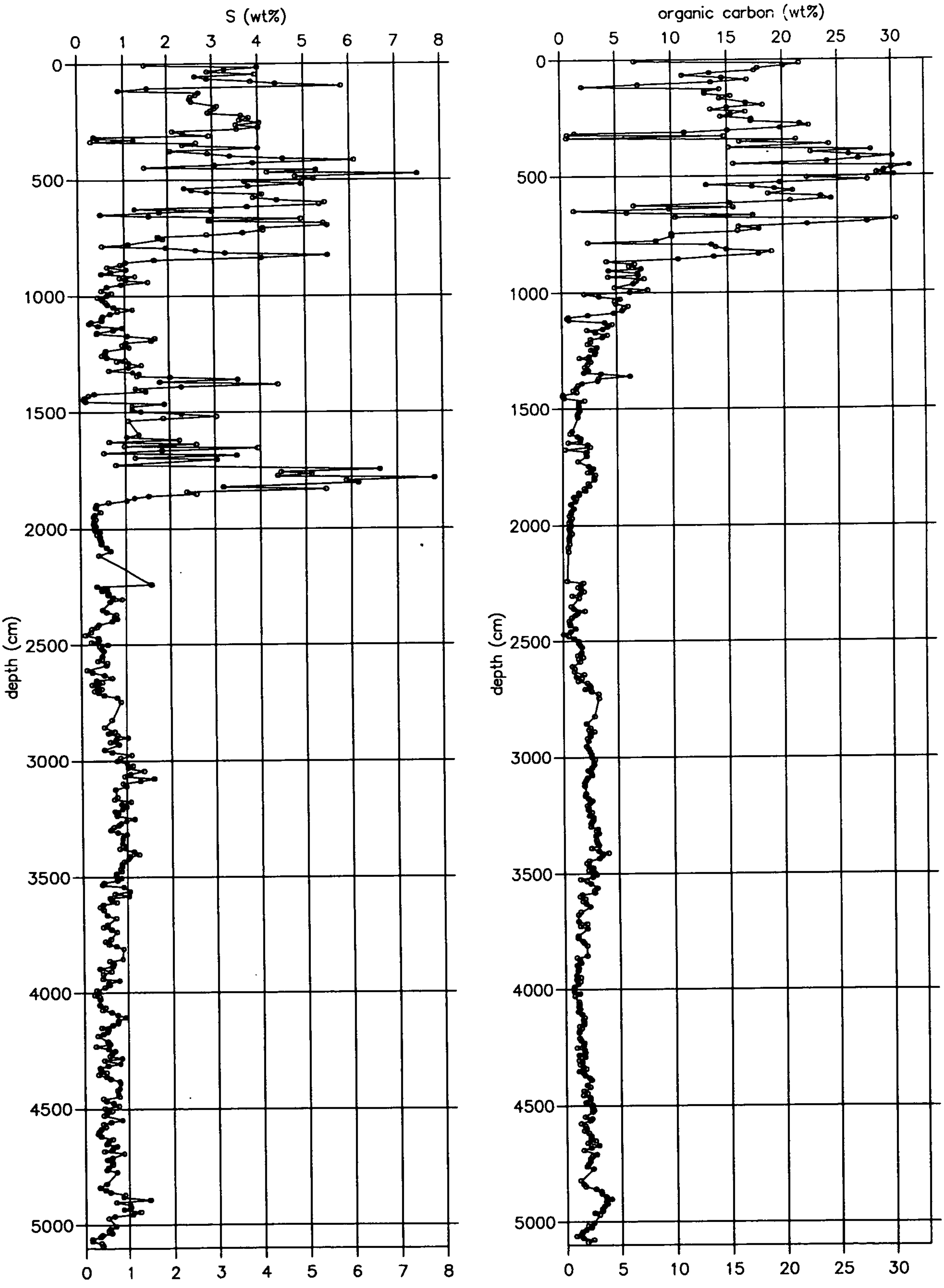


Fig. 4.50. Organic carbon and sulphur

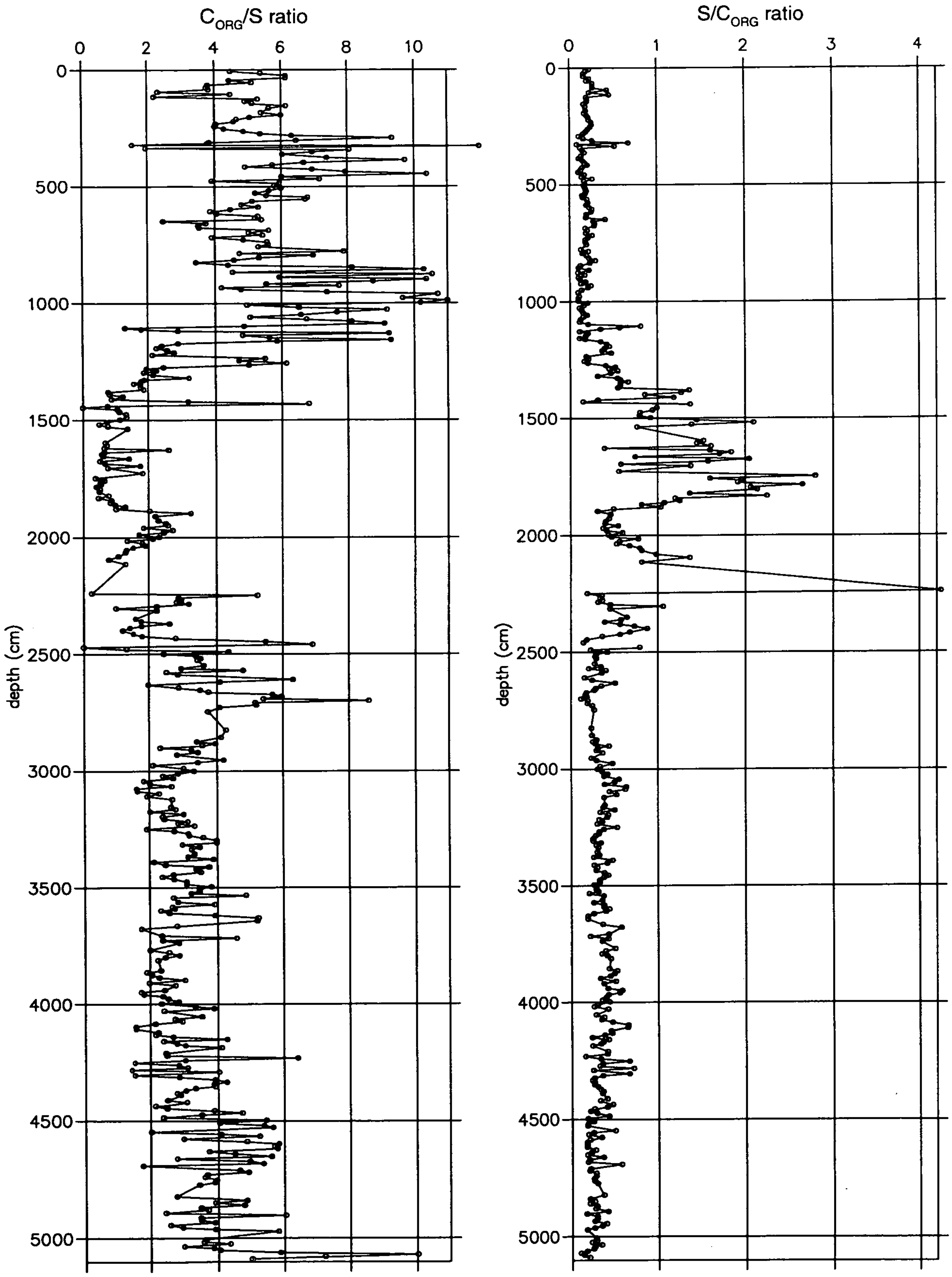
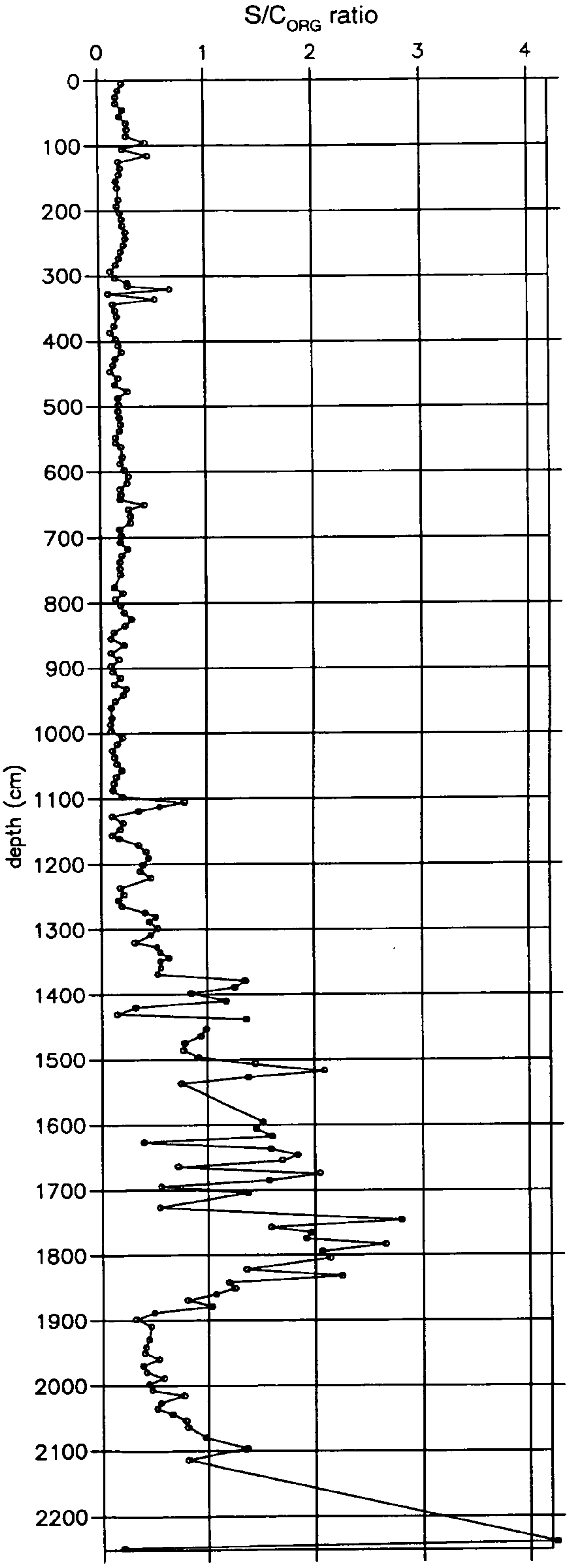


Fig. 4.51. Organic carbon/total sulphur (C_{ORG}/S) ratio and total sulphur/organic carbon (S/C_{ORG}) ratio



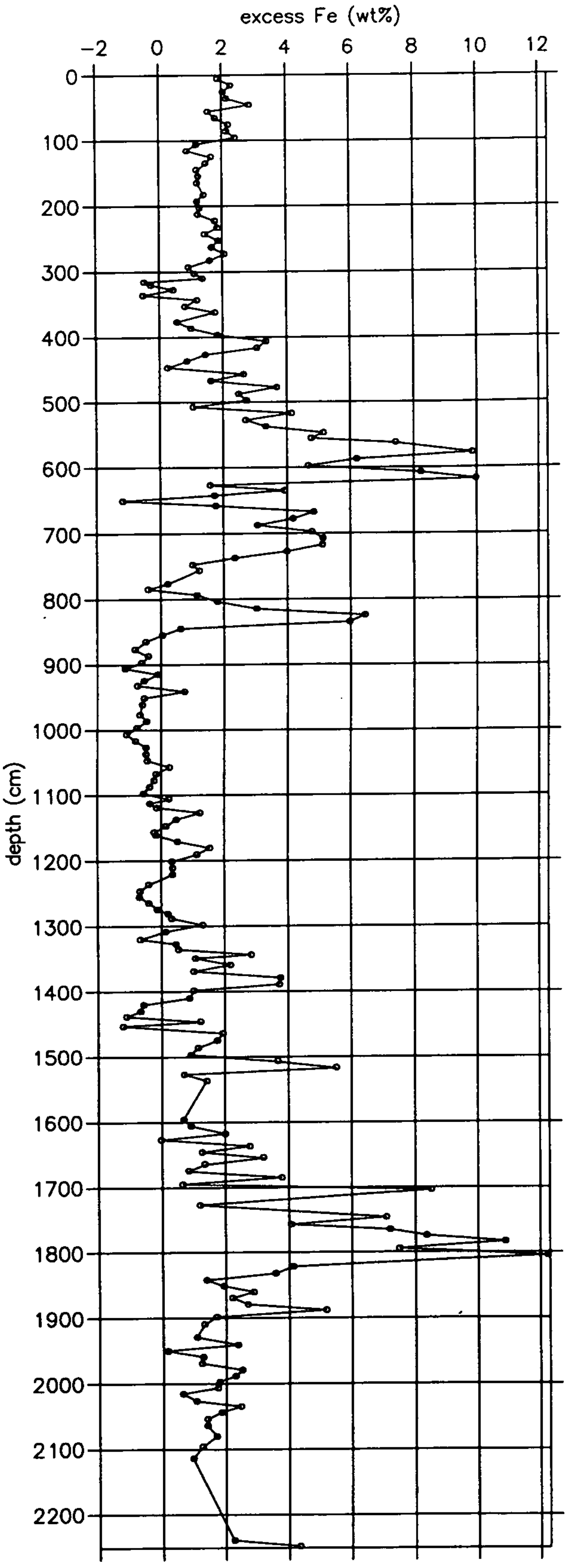


Fig. 4.52. S/C_{ORG} ratio and excess Fe for the upper 2250cm

In Fig. 4.52. a comparison is made between the S/C_{ORG} ratio and excess Fe profiles for the upper 2250cm. High S/C_{ORG} values can be seen to correspond broadly with high excess Fe between 1900 and 1150cm. This correspondence is complicated by the fact that some of the excess Fe is present in siderite here. However, a maximum in iron sulphide (pyrite) content might be predicted between 1800 and 1740cm depth and this is in agreement with the thin section observations described below. Outside this zone, high excess Fe values are mostly thought to reflect vivianite, although some Fe sulphides are likely to be present at 825cm and 30cm depth. The high S/C_{ORG} ratios above 1150cm are clearly associated with tephra layers and the elevated values between 1900 and 2250cm depth are connected with the organic-poor turbidites and basal sand layer (see Chap. 4b). These samples contain little organic carbon, but are relatively unweathered and may hold moderate amounts of S in the silicate mineral fraction.

XRD examination

Bulk sediment XRD analysis detected pyrite in a number of regions of the profile, most particularly between and 1680 and 1810cm depth where strong diffraction spectra were observed. Pyrite was also detected at 4923cm, 2239cm, 1480cm, 825cm, 650cm and in the upper 50cm of the profile. No other forms of crystalline sulphide mineral were discovered, although amorphous Fe monosulphides would not be recognised by this technique.

Thin section examination

One of the most striking features from the microscopic record is the presence of numerous pyrite-rich layers in the sediments between 1600 and 1850cm depth (B.Zolitschka, unpubl. work). The pyrite appears as rounded grains (perhaps framboidal aggregates) and forms dense horizons up to 50μm thick which may or may not be of annual nature. In other parts of the core smaller (generally sub-micron sized) black grains are visible, but it is not possible to determine whether these are sulphide minerals or oxides of iron.

Discussion

Sulphur may be supplied to lakes through the weathering or erosion of catchment rocks and by atmospheric deposition of SO_4^{2-} (Drever, 1982). In many settings the catchment lithologies contain little sulphur and the influence of acid rain SO_4^{2-} deposition has been studied in detail (Rudd et. al., 1986; Nriagu and Soon, 1985). In Lac du Bouchet where the basaltic and granitic catchment rocks contain 'little sulphur or chlorine' the atmospheric supply was judged to be dominant (Truze, 1990). However, certain crater lakes have been associated with extremely high levels of sulphur attributed to local sources. For example, Lein et. al. (1970) describe sediments containing over 50wt% S in lakes where hydrothermal supply is particularly important. In Lago Grande di Monticchio it was shown in Chap. 2 that the catchment rocks contain substantial S (in the form of sodalite-haüyne minerals and perhaps groundmass material). It is believed here that catchment supply represents the dominant source and that this has often led to high S concentrations in the lake.

Sulphur might be transported from the catchment in solution (as dissolved SO_4^{2-}) or in connection with particulate material. The latter might include S bound in terrestrial organic matter (either through primary assimilation or by secondary complexation) or possibly sulphide minerals (such as pyrite) which may have formed under reducing conditions in the soil. The S supplied in these ways could either be 'locked away' in the sediment on deposition or be available for further reactions in the lake waters.

Sulphate reduction appears to represent the most important process for removing sulphur from aquatic systems and fixing it to the sediments (Rudd et. al., 1986). This may occur through the formation of iron sulphides and/or the formation of organic sulphur compounds. These two pathways will be discussed in turn.

The formation of pyrite and Fe monosulphides has been described by many authors (Berner and Raiswell, 1984 and refs. therein). The process occurs under anoxic conditions either within reducing sediments (Morse et. al., 1992) or in anoxic bottom waters with subsequent depositional settling (Lyons and Berner, 1992). As a generalisation, freshwater sediments tend to contain lower amounts of sulphide minerals than marine or hypersaline settings due to the lower availability of dissolved sulphate (Postma, 1982; Jones and Bowser, 1978). This represents just one factor limiting the amount of Fe sulphides that can form. The other main factors are the availability of Fe and the presence of reactive organic matter. Freshwater sediments have been classified as environments where the availability of dissolved sulphate is the key limiting factor (Berner and Raiswell, 1984). These authors proposed the use of C_{ORG}/S ratios, albeit with some assumptions, as a palaeosalinity index. This notion was later re-examined by Davison et. al. (1985) who recommended the usage of C_{ORG}/pyrite S ratios as a more sensitive indicator.

Fe monosulphides (otherwise known as acid volatile sulphide or AVS) represent a thermodynamically unstable phase relative to pyrite (Emerson, 1976). Many studies have found that AVS may be abundant in the near-surface sediment zone, but is rare or absent at depth (Rudd et. al., 1986; Davison et. al., 1985). It is possible that either diagenetic conversion to pyrite takes place during continued burial or the AVS becomes recycled through sulphide oxidation processes (Toran and Harris, 1989). In the English Lake District, AVS was found to form under summer anoxic stratification when high levels of Fe^{2+} and H_2S existed in the bottom waters (Davison et. al., 1985). Pyrite formation might take place through replacement of this early AVS phase or may occur directly, usually under moderately reducing conditions (Zaback and Pratt, 1992). In the Lake District, formation of primary pyrite has been associated with the lower supply of Fe^{2+} and/or H_2S during periods of overturn or O_2 influx (Davison et. al., 1985). Dickman (1985) and O'Sullivan (1983) have described mechanisms by which varve sequences containing pyrite-rich subunits may develop in small 'overdeep' lakes in response to seasonal redox changes. The relative importance of direct and secondary pyrite formation still appears to be a subject under review.

Organic sulphur is generally considered to be of two forms: 1) sulphate esters, and 2) carbon bonded sulphur (Rudd et. al., 1986). Sulphur may become incorporated in plants during their lifetime through biosynthesis (Francois, 1987), although this will not normally lead to high S contents. Typically living organisms contain <2wt% S on a dry weight basis (Jørgensen, 1977). Diagenetic enrichment is thought to be responsible for the higher S contents that occur in some types of organic matter. Stable isotopic and organic geochemical evidence indicate that the processes of enrichment operate by the reaction of **reduced** forms of sulphur (H_2S, polysulphides) with suitable organic matter (Mossmann et. al., 1991; Kohnen et. al., 1989; Nissenbaum and Kaplan, 1972). Humic and fulvic acids may represent the main organic phases involved, although other classes of organic compound are also capable of incorporating sulphur (Nriagu and Soon, 1985 and refs. therein). Diagenetic enrichment could take place both in the catchment soil environment and in the lake waters or sediments under conditions of oxygen depletion. However, most studies indicate that the main focus for S-enrichment is within the lake sediment zone. For example, Nriagu and Soon (1985) found that the C_{ORG}/S ratio of lake seston was 23, but the C_{ORG}/S ratio of the surface sediments was as low as 3.3 for McFarlane Lake, Ontario. (In this setting total sulphur was believed to reflect mainly organic S.)

Many (but not all) of the recent studies have emphasised the importance of organic sulphur as a long term sink in sedimentary environments. The presence of over 50% of total sulphur in organic forms has been noted (Ferdelman et. al., 1991; Nriagu and Soon, 1985). A more critical view is taken by Carignan and Tessier (1988) who suggest that reactive Fe is an abundant element in many anoxic environments and should preferentially utilise reduced sulphur. The formation of iron sulphides and organic sulphur may reflect two competing processes. It appears, hovever, that Fe sulphides and organic sulphur may develop at similar times in some lake environments (Rudd et. al., 1986). The latter authors found that higher percentages of Fe sulphide (particularly AVS) became remobilised during a subsequent overturn event and organic sulphur was found to dominate the long term sediment record because of its higher preservation potential.

Interpretation

The unusually high sulphur contents of the Monticchio sediments are attributed to the S-rich volcanic catchment zone. This has led to high levels of S in the organic matter throughout the record and in some periods high contents of pyrite too.

The develpment of sulphur-rich organic matter is thought to have taken place mainly by diagenetic enrichment with primary biosynthetic incorporation of secondary importance. The C_{ORG}/S ratios for the Holocene period are thought to be dominated by contributions from the organic matter as evidence suggests low Fe sulphide contents. In this area the C_{ORG}/S ratios of between 4 and 6 may represent the sulphur saturation capacity for the organic matter. It is thought that organic matter may incorporate S to a minimum C/S of around 5 (Bein et. al., 1990). The Holocene values are therefore close to this limit. The even lower C_{ORG}/S ratios between 1150 and 1900cm depth are clearly influenced by varying amounts of inorganic sulphur. It is also thought that C_{ORG}/S ratios of between 2 and 6 for the sediments below 2250cm depth are influenced by some contribution from inorganic sulphur, perhaps minor amounts of pyrite.

The formation of diagenetically enriched organic matter is thought to have taken place in the hypolimnion environment and/or in the surface microlayers. Formation of H_2S from sulphate reduction in deeper burial zones conflicts with the presence of early formed vivianite and siderite in several areas, the latter associated with Mn-enrichments. It is thought that an alternation of oxic and reducing conditions provides the most likely explanation for this trend. Sulphate reduction is predicted as being confined to a very shallow zone above the region of siderite or vivianite formation at these times. The process of organic sulphur enrichment was probably most active close to the sediment-water interface during periods of anoxic stratification.

The existence of this process has implications for the process of diagenetic nitrogen enrichment which may also have operated. It is possible that the lake waters contain reasonably high levels of dissolved NO_3^-, also a result of the unusual catchment geochemistry (Chap. 2). This may have enabled ammonium to be produced by microbial activity and incorporated into the organic matter. This process is not considered to be as dramatic as that for S, but it may explain some of the low C/N trends described in Chap. 4a.

If this is correct, the C/N ratios reflect a combination of primary source characteristics and diagenetic enrichment, precluding a straightforward source dominated interpretation.

The presence of substantial excess Fe contents during various parts of the record suggests that reactive Fe is probably available in the sulphate reducing environment. It might be expected that Fe sulphides would form in preference to organic S under such conditions. Perhaps significant quantities of *labile* Fe sulphides formed rapidly during the H_2S production periods. This may have depleted the levels of Fe available encouraging organic sulphur to develop as well. It is proposed that if this did occur then almost all of the Fe sulphides tended to be recycled leaving organic S preserved. The black sediments between 500 and 850cm would represent a time when some of the AVS was preserved. Pyrite *may* be present almost continuously in the sediment record, but it must often occur in trace amounts. This might represent low rates of formation within the lake or limited transport of the mineral from catchment soils. On the other hand, the apparent pyrite dominated zone around 1800cm reflects a time when Fe sulphide formation was greater in terms of production and/or preservation. It is not certain whether this was promoted by increased loadings of Fe and S to the lake system or by variations in redox regime.

The high sulphur contents between 1900 and 1150cm depth succeed the period of turbidite deposition thought to reflect a major disturbance to the catchment (Chap. 4b). This temporal relationship suggests that a large scale erosion of the catchment may have exposed new S-rich pyroclastic material for weathering. At first, conditions may have been too oxygenated or the presence of organic matter too low for sulphate reduction. As the turbidite deposition period declined, it is possible that increased weathering processes released increasing levels of sulphur (and probably Fe) to the lake. At the same time, renewed organic productivity may have created a diagenetic environment conducive to high rates of sulphate reduction during certain seasons. This prompted the formation of layers rich in pyrite at this time. The decline in sulphur between 1740 and 1150cm is thought to reflect the removal of much of this S and Fe loading to the sediment system. Also, decreased accumulation of organic matter (Chap. 4a) may have caused a decline in the rate of sulphate reduction and discouraged pyrite formation. A return to much higher productivity during the post-glacial period is reflected by organic S dominated sulphur removal. Excess Fe accumulation at this time seems to have been controlled by vivianite formation rather than significant sulphide formation.

In order to fit with the mechanism for Mn-rich siderite formation described earlier in this chapter it is necessary for pyrite formation (and S-enrichment of organic matter) to take place either in the hypolimnion and sediment-water interface layer during periods of oxygen deficiency OR in a narrow zone between an Fe oxyhydroxide surface layer and underlying horizon of siderite formation during aerobic periods. The latter requires a strong diffusional limit on the depth of sulphate penetration and resulting sulphate reduction. It is unclear which of these mechanisms is responsible from the generally low resolution information available at present.

There seems to be considerable scope for further work on the behaviour of sulphur in this geochemically unusual setting. This might include the use of ^{35}S as a tracer of recent processes and examination of $\delta^{34}S$ ratios in the sediment system. It will also be necessary to fully investigate the sub-millimetre relationships between iron sulphides and other Fe phases, such as siderite, to better constrain their formation mechanisms.

GYPSUM

XRD examination of sediments from 1750 to 1800cm depth and from the uppermost 50cm of the core revealed the presence of gypsum. Calcite and pyrite also occur in both these zones and an assemblage of gypsum with calcite might be taken to imply the early development of an evaporitic system (Eugster and Hardie, 1978). However, no evidence for gypsum appears in the thin sections which were prepared from freshly extruded core material and it is known that gypsum can form through sulphide oxidation and the resulting consumption of calcite in sediment cores during storage (P. Francus, pers. comm.). This is believed to have occurred here and the gypsum will not be treated as an original mineral.

TRACE METAL ENRICHMENTS

According to Wetzel (1975) the understanding of trace metals in lake systems is at an early stage. Recent studies have improved this understanding of trace metal behaviour (Hilton et. al., 1988). However, most of the new data is centred on historic time scales and the identification of anthropogenic pollution (Hamilton-Taylor and Willis, 1990; Tessier et. al., 1989). Studies of longer sediment records have described trace metal enrichments, but often do not relate the processes involved in these enrichments to palaeoenvironmental change in a clear way (Horie, 1972-1981). Many trace metals are known to be essential as micronutrients (in small quantities), however the large enrichments often observed in organic sediments are normally attributed to diagenetic processes rather than the straightforward incorporation of primary biosynthetic contributions alone (Wedepohl et. al., 1978). There are many possible enrichment mechanisms including the precipitation of discrete mineral phases (e.g. sulphides or carbonates), surface adsorption (e.g. onto Fe-Mn oxides, organic matter or

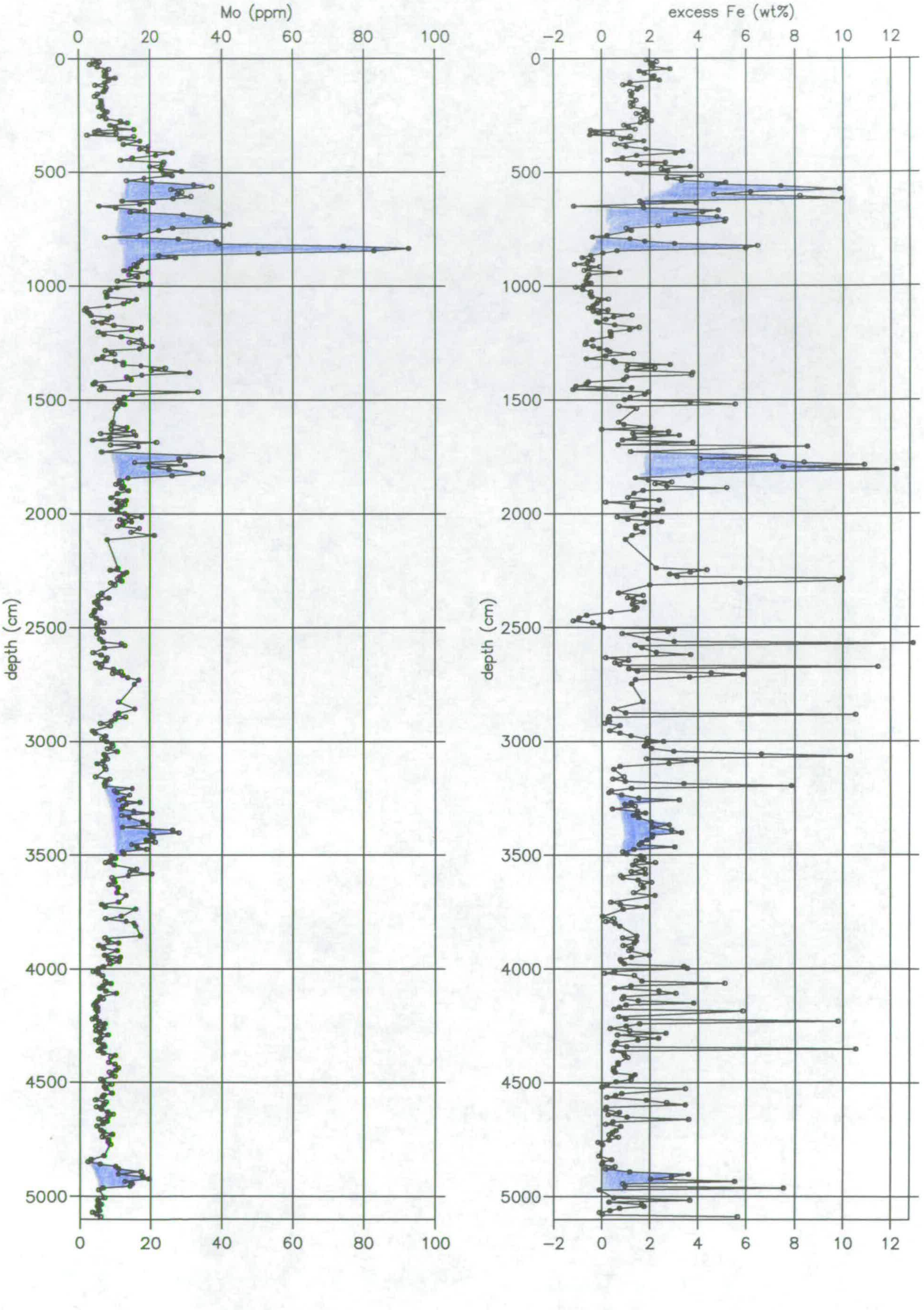


Fig. 4.53. Mo and excess Fe

clays) and complexing into organic compounds (Krauskopf, 1967). It can often be difficult distinguishing which of these pathways predominates and this may hinder the recovery of detailed palaeoenvironmental information, particularly from older records. In addition to the mechanisms of enrichment or fixation it is also ncessary to consider the supply of these elements. This will be related to their availability in the catchment zone and the effectiveness of weathering or erosional processes.

As stated in the multivariate data summary (Chap. 3) a number of trace metals in the Monticchio profile are thought to be influenced by diagenetic mobilisation at certain times. Enrichments appear to be associated with the presence of high organic matter or excess Fe contents. For example, the Mo profile (Fig. 4.53.) shows a pronounced enrichment of <90ppm between 850cm and 800cm depth. Above this horizon the Mo concentration declines exponentially towards the 10ppm level. Below 850cm, concentrations are usually low (<15ppm), although secondary maxima appear to be present at 1750, 3400 and 4900cm depth. These maxima correspond with both organic carbon maxima (Fig. 4.1.) and certain of the excess Fe maxima (see blue shading in Fig. 4.53.). However, the spikes in excess Fe reflecting siderite rich areas are not matched by Mo peaks and it would at least seem likely that the Mo is not associated with an iron carbonate phase.

Mo is known to accumulate in living plants owing to its physiological benefits, particularly as a biocatalyser for nitrogen fixation (Bortels, 1930). Nevertheless, the form of enrichment observed suggests that diagenetic processes have played a role in enhancing Mo content. Two of the major mechanisms of uptake are coprecipitation with Fe sulphides and fixation by adsorption or complexation in organic rich sediments (Pedersen et. al., 1988). Both mechanisms would seem possible since the areas of enrichment are ones of elevated organic carbon content and are believed to contain Fe sulphides from XRD studies (i.e. samples at 825, 1680-1800 and 4923cm depth showed pyrite). King (1991) also found a peak in Mo associated with the onset of high productivity and seasonal anoxia in a lake undergoing brackish to freshwater evolution in Canada. It was claimed that these conditions led to the precipitation of MoS_2 in a black AVS bearing horizon. A change to more reducing conditions in the zones of Mo-enrichment at Monticchio might also be envoked. It is possible that during the initial period of high organic productivity (at 825cm depth) there was a relative abundance of Mo which had been released from the catchment. The reducing nature of these sediments and/or the presence of sulphate reduction would have promoted Mo to be enriched at this time.

The exponential decline in Mo above 800cm depth may be related to a gradual decline in Mo supply from the catchment, either through reduced erosion or general depletion from leaching. This follows a similar explanation to that for early Holocene vivianite maximum discussed in a previous section. It is interesting to note that the zones of maximum vivianite and molybdenum concentration occur in different time planes illustrating how elements may respond differently to the conditions of diagenesis. Mo has been considered to be a relatively mobile component (Wetzel, 1975) and may have been removed from the catchment more rapidly than Fe (which is thought to control the vivianite enrichment trend). It is also possible that Mo was in demand by nitrogen fixing organisms, such as blue-green algae, during the onset of high organic productivity. At this time nitrogen may have rivalled phosphorus as the limiting macronutrient. Perhaps, after the Mo supply declined, it was possible for later photosynthetic organisms to switch to alternative micronutrients for support of their N_2 fixing requirements.

The trends shown by Mo are followed to some extent by Zn, V, and U although these elements are more conservative and tend to be dominated by changes in terrigenous clastic sedimentation. Zn and V are often associated with Fe, and U with organic matter during diagenetic enrichment (Wedepohl et. al., 1978), but it is difficult to determine the exact associations. When ratios to Al are examined these elements all show primary enrichments during the early Holocene and secondary maxima around 1750, 3400 and 4900cm depth.

The upper 1000cm of the Monticchio record is examined in more detail for a number of trace elements in Fig. 4.54. and Fig. 4.55. This zone includes the sharp diagenetic enrichments of the late-glacial to early Holocene period and possible anthropogenic enrichments during the late Holocene. The elements are presented as ratios to Al, and the Fe/Al ratio is also shown for comparison. It can be seen that Mo, V, U, Zn, and to a lesser extent Pb, Cu and Cr show enrichments parallel to that for Fe between 850 and 500cm depth. The enrichments for Pb, Cu and Cr are very much exaggerated by using ratios to Al, and if normal concentration plots are shown (Fig. 4.56.), the trends of these elements appear virtually indistinguishable from those of other clastic indicators. This is also indicated by the PCA examination (Fig. 3.3.). It can be seen here that Pb, Cu and Cr are situated within or close to the group of conservative mineral clastic elements.

Possibilities exist that the elements shown may be incorporated into the vivianite lattice, be present as trace sulphide minerals, occur adsorbed onto other forms of Fe (such as unreduced Fe(III) phases), or be complexed with organic matter. It is difficult to recognise the precise association mechanism(s) without extractive chemical analysis. Although similar in

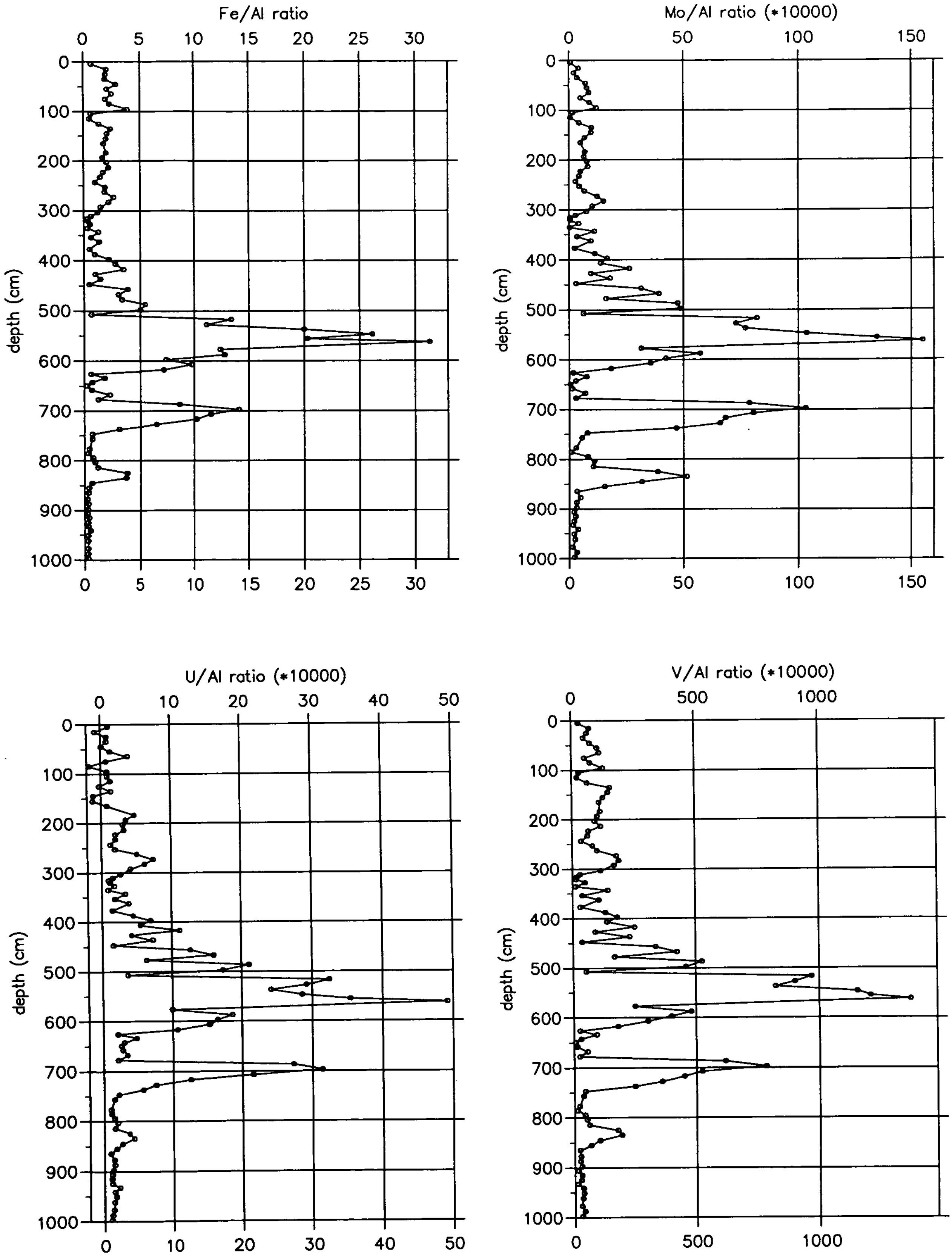


Fig. 4.54. Fe/Al, Mo/Al, U/Al and V/Al ratios for the upper 1000cm

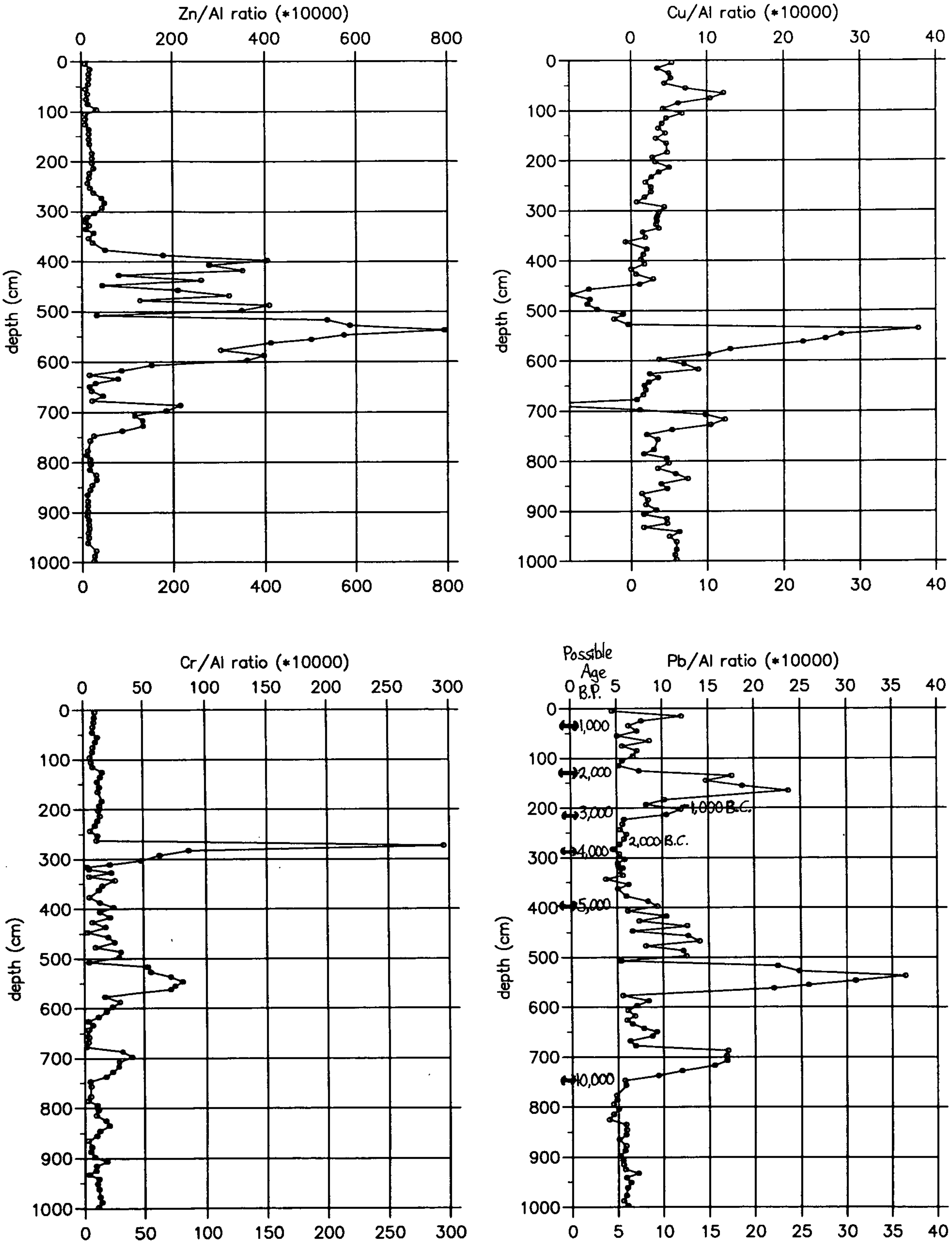


Fig. 4.55. Zn/Al, Cu/Al, Cr/Al and Pb/Al ratios for the upper 1000cm

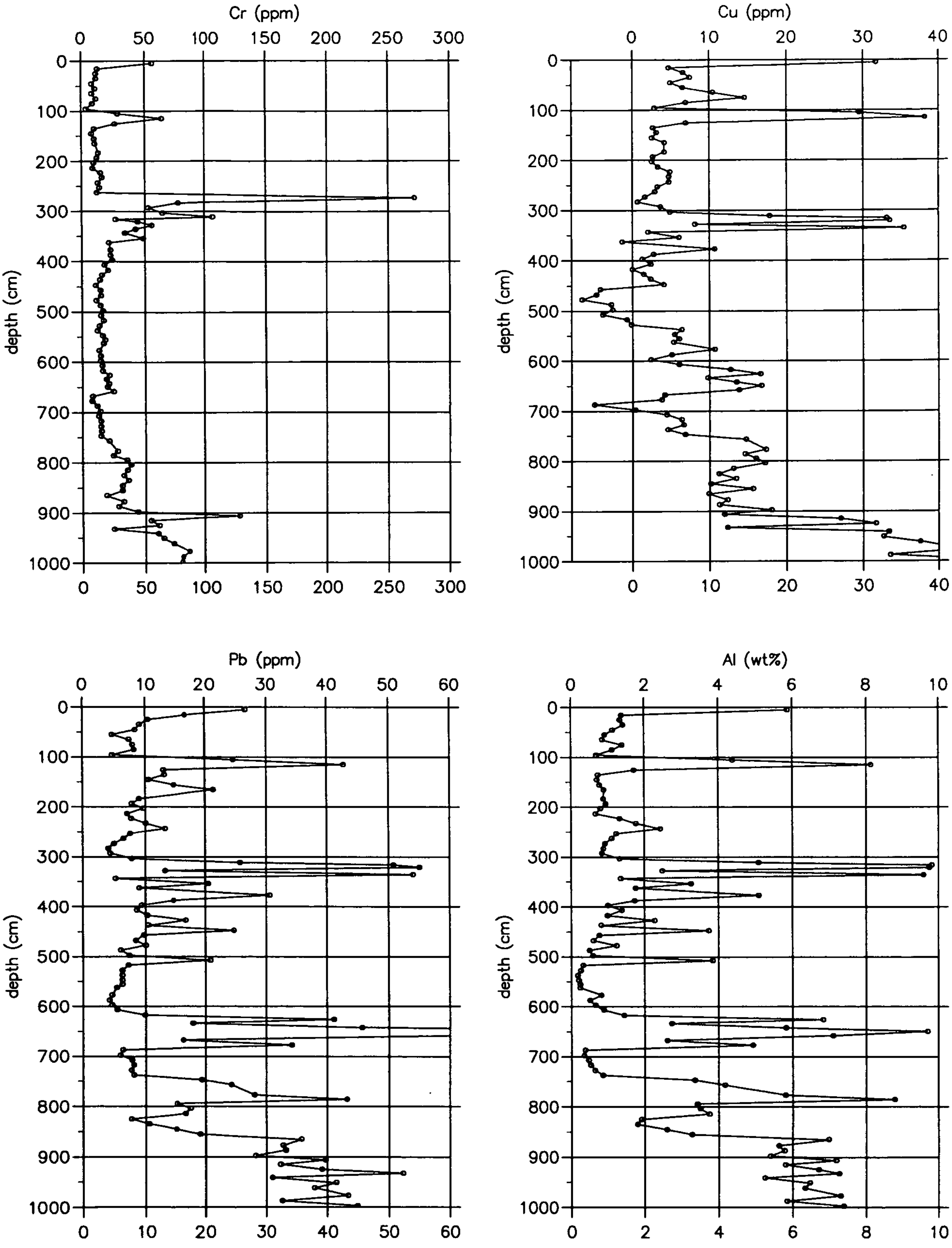


Fig. 4.56. Cr, Cu, Pb and Al content for the upper 1000cm

overall trends, certain differences in mobility seem to exist. For example, Mo/Al has a relatively high enrichment during the earliest maximum around 825cm. This is illustrated more clearly by the Mo concentration profile in Fig. 4.53. In constrast, the Zn/Al ratio shows little increase at 825cm, but appears significantly elevated at 550cm depth and persists until 350cm. This contrasts with the other elements which fall sharply towards background levels after 450cm.

The upper 300cm contains notable elevations in Pb/Al (220-115cm), Cr/Al (310-270cm) and Cu/Al (95-50cm). Ratios of elements such as Pb/Al have been used in palaeoenvironmental studies to identify anthropogenic effects (Brenner et. al, 1991; Bruland et. al., 1974). It is thought that the enhanced ratios, particularly that of Pb, may reflect cultural activity at Lago Grande di Monticchio since they are not readily correlated with tephra layers or diagenetic phases. It has been speculated that the tephra layer around 115cm depth may represent the eruption of Mt Vesuvius in A.D. 79 (A. Newton, pers. comm.). If this is taken to be correct, and the Holocene boundary assumed to lie at 750cm depth, the period of Pb enrichment interpolates at around 3000 to 2000 years B.P. (i.e. 1000 to 0 years B.C.). This may be coincident with the rise in Roman civilisation. However no other evidence is yet available to demonstrate activities such as metal smelting in the Monticchio catchment and it is not clear whether a local source of ore material would be available for these purposes. The Cr peak would equate at around 2000 years B.C. using this timescale and perhaps be related to human activities in the Bronze Age. The presence of local Bronze Age sites was desribed in Chap. 2 and it is possible that Cr was present in metals that were again introduced to the catchment. The Cr peak follows a tephra zone at 325cm depth and might alternatively be connected with Cr supplied this way, but it is thought that the tephra layers are in general relatively Cr-poor. The Cu peak equates to an early Medieval or Dark Ages period using the above estimations. This may have reflected another phase of human occupation. Hopefully varve counting work and observations of charcoal in the thin section record will improve the correlation of these proposed events.

The last few 100 years are absent from the top of this record, but it is predicted that these sediments would show a renewed increase in the content of certain trace metals, particularly pollutants. The 0cm level of this core may therefore terminate in the late Middle Ages or Elizabethan period (i.e. within the pre-Industrial Revolution era).

SUMMARY OF MAJOR DIAGENETIC REGIONS

The following divisions are made as a broad diagenetic characterisation of the sediment record:

5100 to 2250cm
mainly siderite in minor quantities, but locally high
traces of calcite and pyrite
minor vivianite, particularly during biogenic dominated periods (3400 and 4900cm)

2250 to 1900cm
mainly calcite in moderate to high quantities
traces of pyrite

1900 to 1650cm
high contents of calcite, siderite and pyrite
minor vivianite

1650 to 850cm
minor vivianite, pyrite and locally calcite
minor siderite below 1100cm

850 to 500cm
high contents of vivianite
some pyrite and AVS also present

500 to 0cm
minor pyrite and traces of vivianite
minor calcite in upper 50cm

Brief comments:
The zone between 5100 and 2250cm is thought to represent a relatively stable environment prior to the catchment disturbance event at 2250cm. Siderite appears to be the normal diagenetic phase, particularly during glacial or intermediate periods It may be elevated due to short term events such as periodic high rainfall and erosion. The postulated climatic optima of 3400 and 4900cm depth (Chap. 4a) are more associated with vivianite and perhaps pyrite.

The zone between 2250 and 1900cm is related to the early period following catchment disturbance when biogenic sedimentation was low, but conditions favourable to calcite precipitation. Calcite may have precipitated periodically in response to temperature changes and later renewed surface productivity. Aerobic decomposition and sulphate reduction processes may have effectively mineralised the majority of organic matter sedimented at this time.

This was followed by a period of greater stability between 1900 and 1650cm when enhanced organic matter accumulation took place. This was connected with the greater supply of Fe, Mn and nutrients from renewed catchment weathering and perhaps a more stable water body. Precipitation of diagenetic Fe phases was driven by organic decomposition in a seasonally fluctuating (oxic/anoxic) hyplolimnion. Ostracods were able to develop in the temporarily nutrient **and** calcium rich waters. Eventually much of the leached Fe, Mn, S and calcium carbonate became removed to the sediments and organic productivity declined (probably due to climatic detrioration).

The zone between 1650 and 850cm has similarities with the lowest zone, in that organic productivity was relatively low and the supply of reactive elements subdued. Local periods of diagenetic enhancement may reflect temporary climatic changes or possibly effects from tephra loadings to the catchment.

The abrupt rise in organic accumulation above 850cm (probably in response to increased weathering and nutrient release) led to a high rate of organic matter turnover in the sediment zone. Large fluxes of phosphate favoured vivianite formation, and sulphate reduction led to the preservation of some Fe sulphides along with large amounts of organic matter S-enrichment. Again conditions appear to have alternated between oxic and anoxic in the lake. The formation of diagenetic Fe phases appears to have come to an end around 500cm, probably due to reduced supply from the catchment.

The upper 500cm is associated with high levels of CO_2 fixation as organic matter and probably high rates of nutrient turnover. Diatom sedimentation was also high and this may not have suffered from the reduced catchment supply (of dissolved silica) as much as the Fe-mineral forming processes. Calcite may have been favoured by a lowering in lake level near the top of the record and perhaps by secondary alkalinity caused by tephra events.

CHAPTER 5

FURTHER INVESTIGATION OF THE ORGANIC MATTER

Introduction

At the time of writing, a study is being made on the lipid fractions from 10 samples in the Monticchio profile. This work involves determination of the abundance and distribution of identifiable aliphatic hydrocarbons, aromatic hydrocarbons, alcohol and sterol compounds, using the techniques of gas chromatography (GC) and gas chromatography coupled with mass spectrometry (GC-MS). In addition, compound-specific isotope ratio mass spectrometry (GC-IRMS) is in progress on selected classes of lipids. An attempt may also be made to carry out a.m.s. radiocarbon dating on certain of the lipid fractions. To compliment this geochemical information (as recommended by Durand, 1980), the palynofacies character of the organic matter has been investigated under the microscope.

PALYNOFACIES INVESTIGATIONS

The palynofacies technique involves the identification and quantification of all forms of particulate organic matter present in a sediment using transmitted light microscopy. This organic matter includes palynomorphs, such as pollen grains and insect remains which may be studied in their own right, together with fragments of structureless/amorphous matter and other plant material (phytoclasts). The palynofacies approach was pioneered by palynologists and has mainly been concerned with ancient sedimentary sequences, especially in the context of hydrocarbon source rocks (Combaz, 1980), and with Cenozoic marine sequences (Bertrand et. al., 1991). However, in a few studies it has been applied to palaeoenvironmental reconstructions of late-Quaternary lake sediment records (Bertrand et. al., 1992; Talbot and Livingstone, 1986).

A set of 10 unground sediment samples from key areas of the profile were prepared for palynofacies investigation (see Appendix 1). The sample locations are shown for reference on the organic carbon profile in Fig. 5.1. Basic point counting work (of between 140 and 500 counts per sample) on the material suggests various trends which have been expressed as a percentage chart (Table 5.1.). From these results some simple qualitative observations and interpretations may be made concerning the source and state of preservation of the organic matter. These can be compared with the bulk geochemical parameters previously determined on each sample (Table 5.2.). Absolute concentrations of the palynofacies components have not been determined and so trends in Table 5.1. reflect relative changes in the material present.

The two most abundant components of the organic matter assemblage are amorphous organic matter and 'plant material'. The former is generally linked to algal sources and the

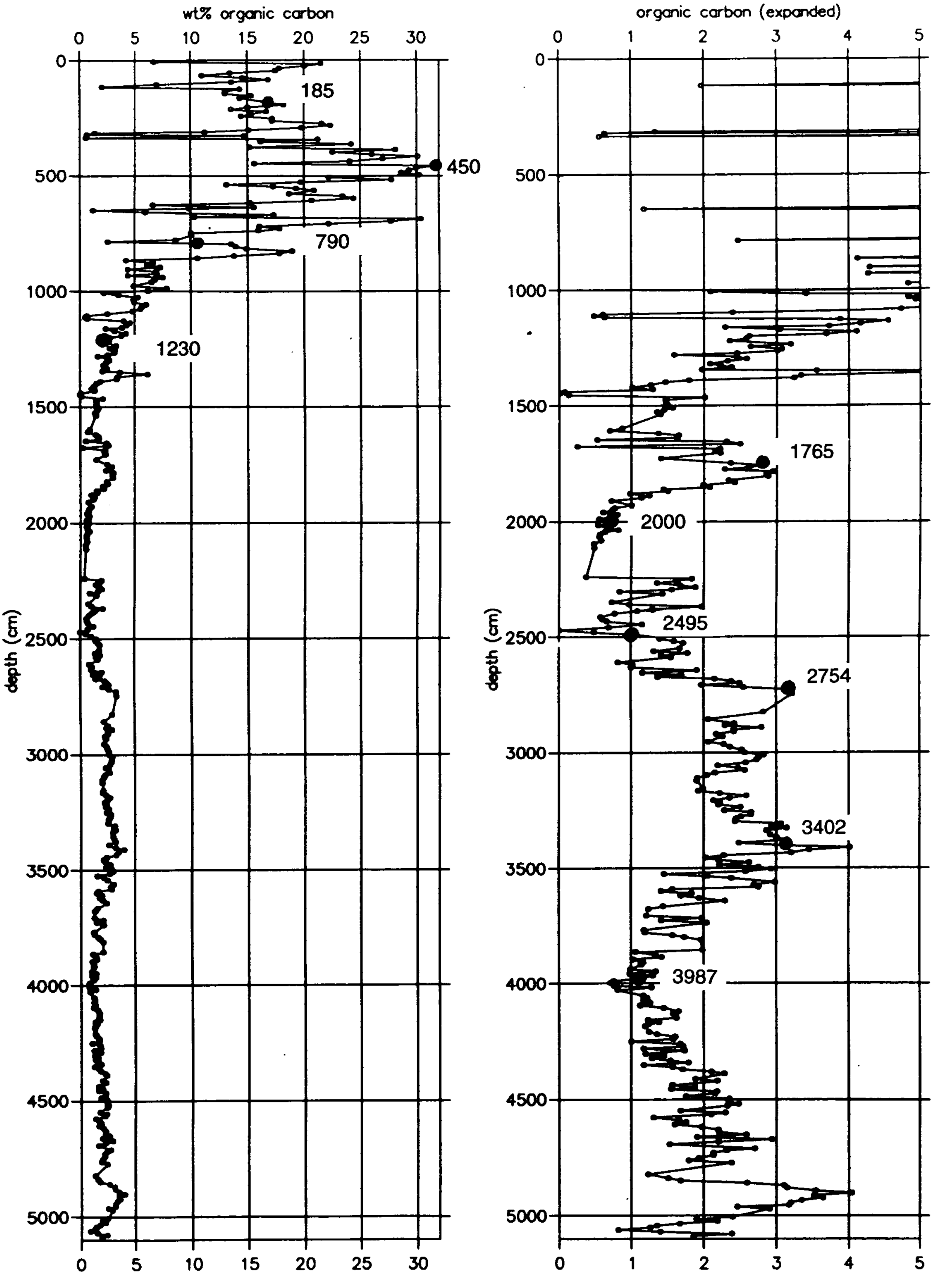


Fig. 5.1. Organic carbon content and samples selected for palynofacies examination

Sam	AOM	plant	gel	am'd	polSp	fung	zooCl	chir	clad	ped	bt
185	46	15.5	2.4	6.9	9.6	4.1	12.4	0.3	2.1	----	----
450	37	20.0	8.0	10.3	13.7	4.0	6.6	----	0.3	----	----
790	41	14.0	0.9	7.2	9.5	3.6	18.0	0.9	0.9	3.2	0.5
1230	38	11.5	2.8	19.1	8.1	2.2	15.2	0.4	0.6	0.4	1.8
1765	58	7.0	1.5	5.6	13.0	1.9	9.6	0.9	0.9	----	1.5
2000	80	8.5	0.7	4.9	2.8	1.4	1.4	----	----	----	----
2495	64	7.0	2.4	12.2	6.9	3.7	2.0	----	0.4	----	1.2
2754	60	12.0	0.4	8.0	10.5	3.8	4.6	0.4	----	0.4	0.4
3402	49	19.5	0.9	4.0	11.1	3.4	7.1	2.0	1.7	0.6	0.6
3987	74	6.5	3.3	3.8	5.8	2.5	3.3	0.4	0.4	----	----

Table 5.1. Percentages of palynofacies components (based on 140-500 counts/sample)

AOM=amorphous organic matter
plant=(wood+cuticle+plant tissue)
gel=gel-like degraded matter
am'd=amorphous degraded matter
polSp=(pollen+spores)
fung=fungal material (hyphae)
zooCl=zooclasts (e.g. insect leg fragments)
chir=chironomid remains
clad=Cladocera
ped=*Pediastrum*
bt=*Botryococcus*

Sam	TOC	C/N	HI	BSil
185	16.75	9.4	408	54
450	31.66	10.9	380	28
790	13.58	4.5	267	41
1230	3.19	10.3	316	29
1765	2.62	9.7	120	17
2000	0.68	4.8	68	---
2495	1.42	6.9	135	9
2754	3.22	8.9	183	44
3402	3.13	13.6	192	67
3987	0.76	4.5	95	---

TOC=wt% organic carbon
C/N=C/N weight ratio
HI=hydrogen index
BSil=wt% biogenic silica

Table 5.2. Bulk geochemistry of palynofacies samples.

latter to terrestrial or aquatic macrophyte sources (Bertrand et. al., 1992). The plant component percentage is highest during the Holocene samples (>15%) and also at 3402cm which may be an earlier interglacial period. Comparison with Table 5.2. shows that these samples generally possess the highest C/N ratios (>10). These observations are in accordance with the discussion of C/N ratios and HI values in Chap. 4a. Interglacial-type periods tend to be associated with a relatively high contribution of terrestrial and/or aquatic macrophyte organic matter displaying a good state of preservation. Well preserved amorphous (algal) matter may also be abundant at these times, but not as high in relative terms. In contrast, the glacial periods are associated with lower proportions of terrestrial organic matter (and much lower absolute concentrations) and by a moderate amount of amorphous organic matter which may be in a more degraded state. Hence the increased HI values that would be predicted by the greater contribution from planktonic kerogen types are offset by the overall degraded and poorer quality of the organic matter. This can be appreciated visually by comparing the fresh-looking organic matter in samples 185 and 450 from the Holocene with other samples from lower in the profile (Plates 7-9.). The Holocene samples have HI values around 400 while other samples are generally below 200. Qualitative examination shows the possible Eemian interglacial (covered by the sample at 3402cm) to have a poorer quality state of preservation than the Holocene, but much better preservation than its neighbouring samples. The 1230cm sample contains reasonably high values of C/N and HI together with a relatively high plant component and may reflect an interstadial period during the last glacial cycle.

The lowest percentage of amorphous organic matter is 37%, for the early Holocene sample at 450cm. The generally >40% contribution from AOM suggests that planktonic contributions have been a significant component throughout most of the profile. The lower percentages which often occur in samples with high organic carbon suggest that the main influence has been a dilution effect caused by increased contributions of plant material. The highest amorphous content occurs in a sample from the turbidite zone at 2000cm which contains 80% AOM. This sample should be treated with caution because only half as many 'grains' as normal were available for counting (142 counts were made) and some of the pale 'amorphous material' counted may have wrongly included mineral grains (Plate 8.). Assuming that the value of 80% is accurate, it is suggested that low rates of algal productivity took place at this time and that the organic matter was strongly degraded. Perhaps some fraction of this material survived related to the rapid burial phases of turbidite deposition.

The presence of gel-like organic matter has been interpreted as reflecting the transformation of plant tissue by hydrolysis under reducing conditions (Durand, 1980). This component appears to be most common in the 450cm sample and may indicate appreciable breakdown under anaerobic conditions, perhaps near the sediment surface, during the early Holocene. It is possible that high deposition rates of reactive terrestrial and algal organic matter rapidly consumed oxygen (perhaps during the summer season) and led to significant further degradation by this process. The gelified particles cannot be definitely related to a source, although many of the grain shapes are externally reminiscent of plant fragments such as cuticle pieces. Some gel-like matter is evident in the other samples from the profile, but it is difficult to relate this to environmental change with the small percentage values recorded. Likewise the presence of amorphous degraded matter (i.e. fragments which appear to have been structured at one stage, but now obliterated) is observed, but this is difficult to interpret clearly. It is possible that much of this amorphous material was originally from plant sources. This might perhaps account for the relatively high C/N ratio of the 1230cm sample which contains 19% amorphous degraded matter. The possible relationship with a primary plant source is illustrated by the sample from 2754cm in Plate 8. which shows a fragment of plant tissue at a stage of partial degradation.

The percentage of pollen and spores is generally highest in the interglacial or interstadial periods. This might be expected as vegetation cover is believed to be richer in the catchment region. Values of 10% or more are found at 450, 1765, 2754 and 3402cm depth. The 450 and 3402cm samples are particularly noted for their high levels of bisaccate grains attributed to conifer pollen. It is possible that the pollen and spore figures reflect both the vegetation within the lake catchment and also a contribution from the average regional pollen introduced by atmospheric processes. Detailed palynological information on this record will be provided in the forthcoming publication of work by Watts, Allen and Huntley.

Fungal material, mainly resistant hyphal filaments, is slightly higher during interglacial samples, but does not exhibit a strong trend. Zooclast fragments probably reflect the level of insect life in the lake waters and thus may provide indications on overall trophic status. There is a general trend for higher percentages within the younger part of the record (i.e. the uppermost 2000cm) and a maximum lower in the profile at 3402cm. At these times nutrients may have been elevated and more favourable to supporting a rich community of insect life. More specific indications are provided by the record from chironomid (midge larvae) and Cladocera (water flea) remains. Again there is an overall high level in the upper part of the core and in general during interglacial or interstadial periods. The sample at 3402cm is notable for its high percentages of chironomid and cladocera components. The abundance of these has previously been correlated with interglacial transitions in sediment records from the Eifel

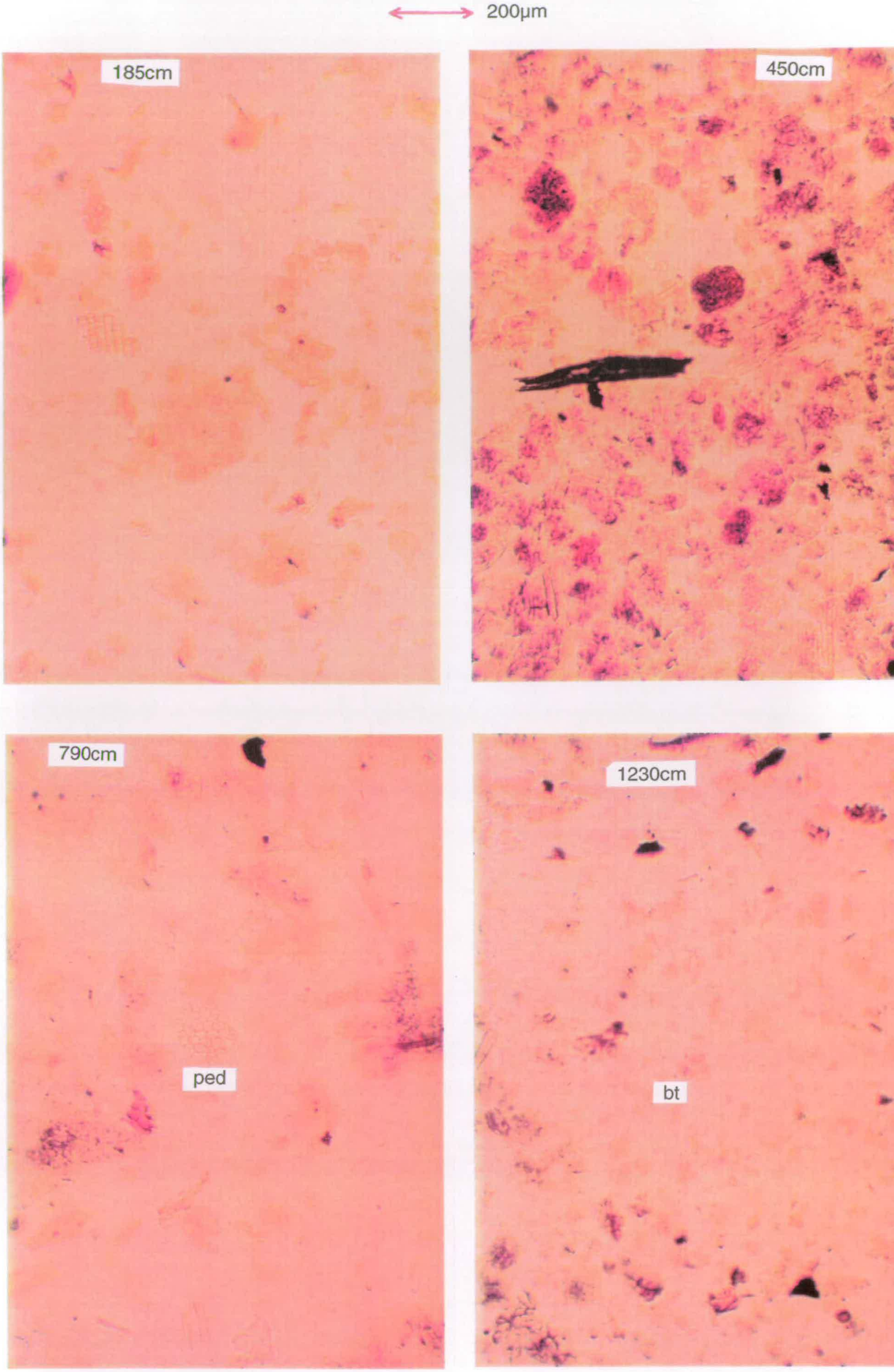


Plate 7. Palynofacies preparations viewed under the microscope.
(ped=Pediastrum, bt=Botryococcus)

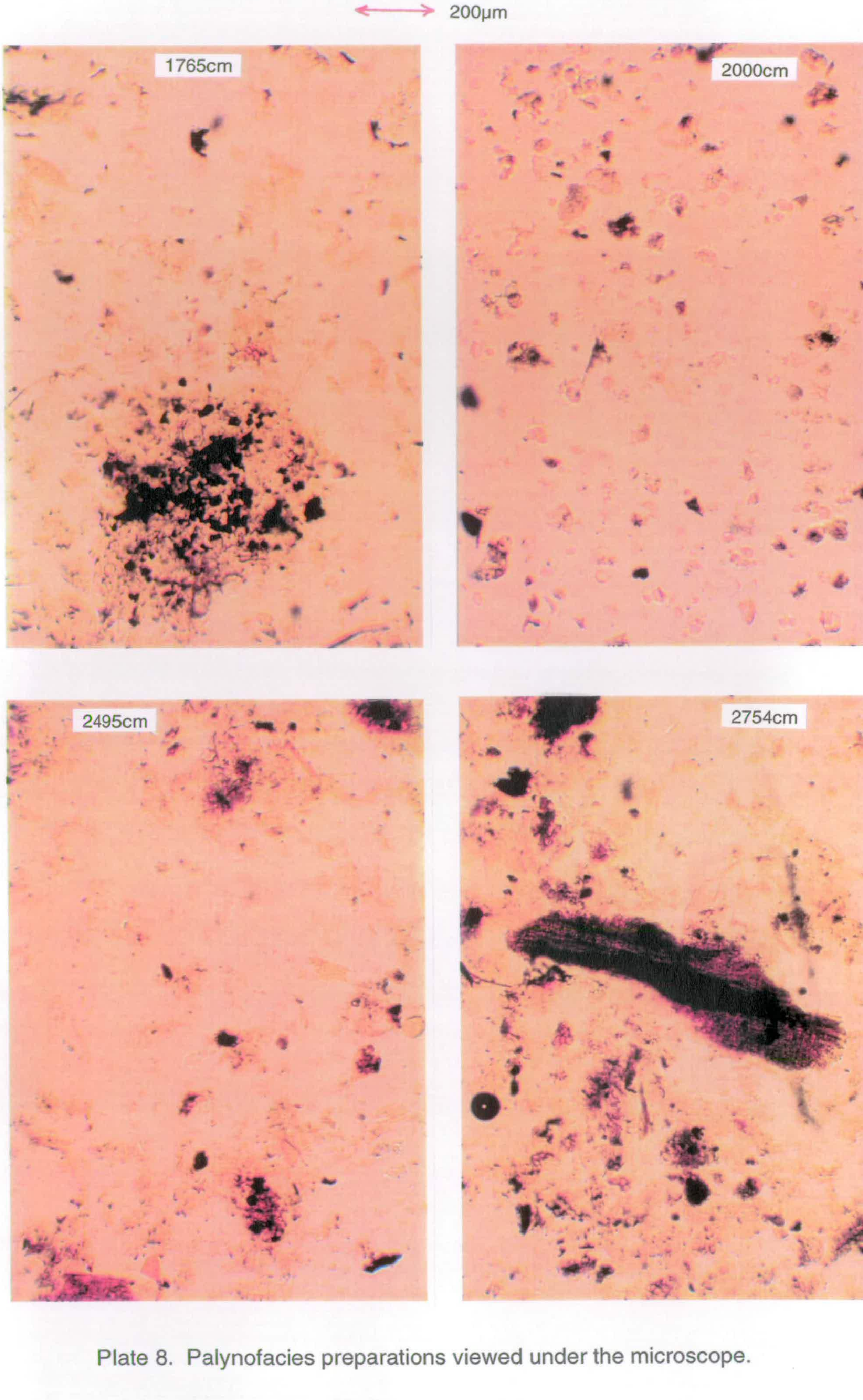


Plate 8. Palynofacies preparations viewed under the microscope.

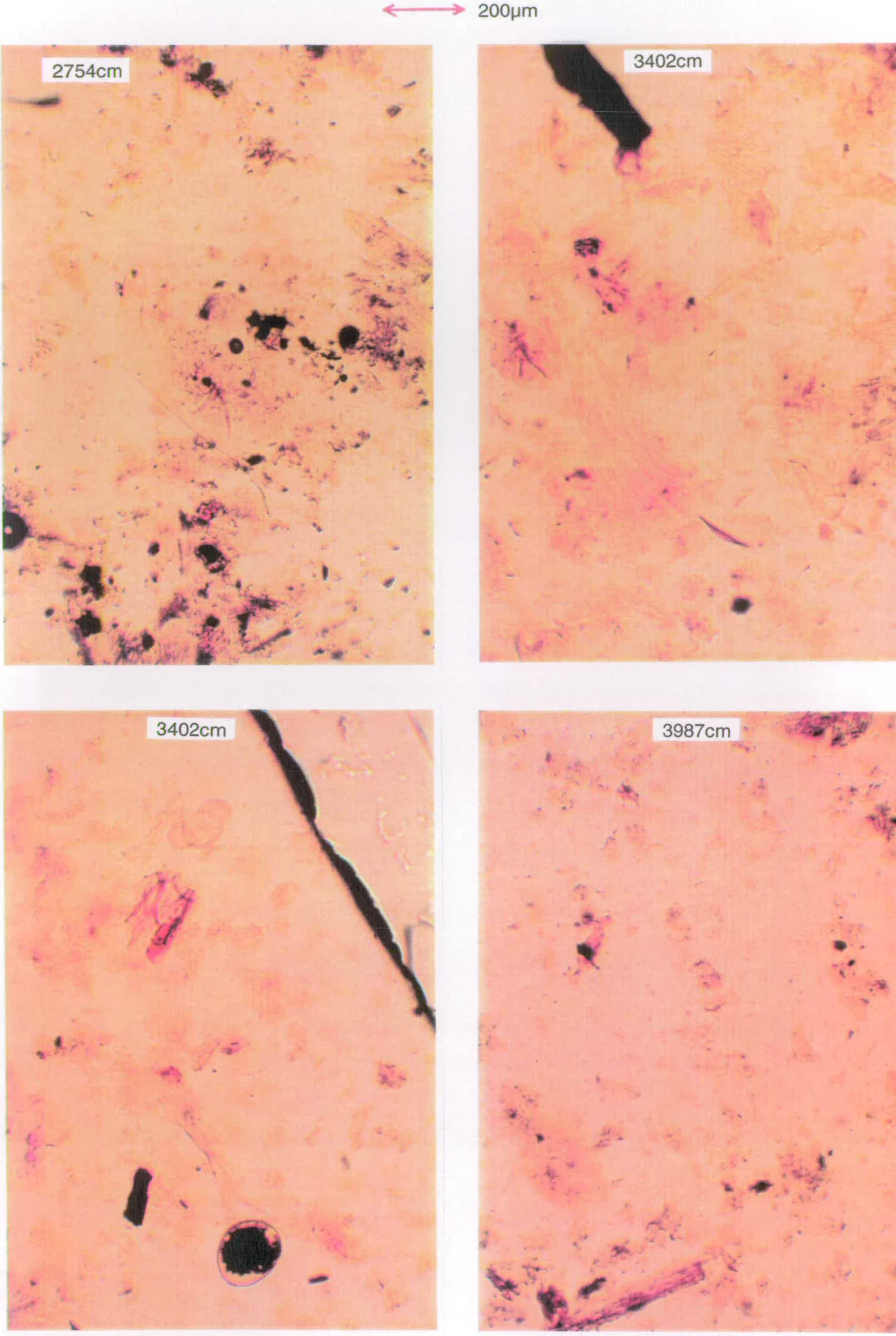


Plate 9. Palynofacies preparations viewed under the microscope.

maar lakes (Hofmann, 1993). However, without species identification this must be interpreted cautiously because certain taxa are more abundant under conditions of low trophic status.

Although most algal material is relatively vulnerable to early degradation and removal, a few algal groups have cell walls made from resistant algaenone compounds, as is the case with the colonial green algae Pediastrum and Botryococcus. The percentages of these algae have been noted in the palynofacies examination and appear to be highest during periods of moderate productivity (i.e. outside the highly organic Holocene period and the particularly organic-poor intervals at 2000 and 3987cm). The presence of these genera have been used to reconstruct trophic status and salinity by some authors (e.g. Hutchinson, 1970). In general Botryococcus is associated with oligotrophic conditions and most species of Pediastrum with a eutrophic state. However, without detailed species identification it is difficult to interpret too far. On the other hand, it is interesting to note that both algae appear related to periods of the Monticchio record where intermediate levels of productivity are thought to have taken place.

In summary, the palynofacies examination has highlighted some *preliminary* trends which provide a useful comparison with the bulk geochemical information. Enhanced levels of plant material, pollen and aquatic insect life appear to be associated with interglacial/interstadial periods and glacial periods appear to be dominated by amorphous organic matter of a degraded nature. The presence of brown gel-like particles and black fusinitic fragments (charcoal?) probably indicate the contribution of allochthonous degraded material. However, it is difficult to reconstruct the relative importance of lacustrine processes from the modest number of samples observed. More information would require a larger number of samples and recounting ot the minor palynomorph components.

The Holocene samples and the sample at 3402cm appear to contain 'fresher' or better preserved organic matter. The amorphous component in these cases is pale yellow or brownish and consists of clean flakes or lumps. In other parts of the record the amorphous matter is more finely divided/granular and dirtier in appearance. Also in these samples other components such as pollen grains and plant tissue more frequently show marked degradative alteration. These differences may be seen in Plates 7-9. The sample from 1765cm shows frequent opaque particles which may be pyritic masses. It would be necessary to produced a polished thin section or apply oblique reflected illumination to confirm this as the black grains do not have classic framboidal aggregate shapes, although they appear irregular in comparison with normal dark woody material. It is thought likely that they do mainly represent pyrite since the geochemical information shown in Chap. 4c indicates that this is a major zone of pyrite occurrence.

ORGANIC GEOCHEMICAL MOLECULAR INVESTIGATIONS

Organic compound classes such as the n-alkanes have long been measured by organic geochemists in order to obtain information concerning the source(s) and diagenetic state of sedimentary organic matter (Eglinton and Murphy, 1969). A number of studies have been made on relatively young Holocene lake sediments, but records extending beyond this are uncommon (Walker, 1990; Cranwell, 1988; Ishiwatari and Ogura, 1984). Where studies have been made logistics usually permit only a limited number of sample points to be investigated in detail due to the lengthy preparation procedures required. In this section some results from the aliphatic fraction (in particular the n-alkanes) are presented and interpretation made in connection with the bulk geochemical data and possible environmental changes. In future additional information will become available on the aromatic hydrocarbon, alcohol and sterol fractions in the same samples. This will assist in an overall interpretation.

Sam	TOC	EOM	eomC	CPI	C/N	HI	BSil
183	16.75	41.63	248.6	24.3	9.4	408	54
457	31.66	62.34	197.0	10.2	10.9	380	28
785	2.47	3.74	151.6	8.3	2.4	142	9
877	6.64	6.84	102.9	12.3	7.8	280	34
951	6.79	12.55	184.8	7.4	8.3	237	26
1236	3.19	5.60	175.6	8.4	10.3	316	29
1794	2.86	5.27	184.3	8.2	9.2	172	22
2445	1.15	0.44	38.6	9.1	9.6	111	---
3317	2.93	9.17	312.9	5.4	16.3	310	66
3412	4.02	4.74	117.9	6.7	14.9	260	63

Table 5.3. Bulk geochemistry of samples studied for lipids including CPI's for alkane fractions.

TOC=wt% organic carbon
EOM=extractable organic matter (mg total lipid/g dry sediment)
eomC=EOM/TOC (mg total lipid/g organic carbon)
CPI=Carbon Preference Index (after Bray and Evans, 1961)
C/N=C/N weight ratio
HI=hydrogen index
BSil=wt% biogenic silica

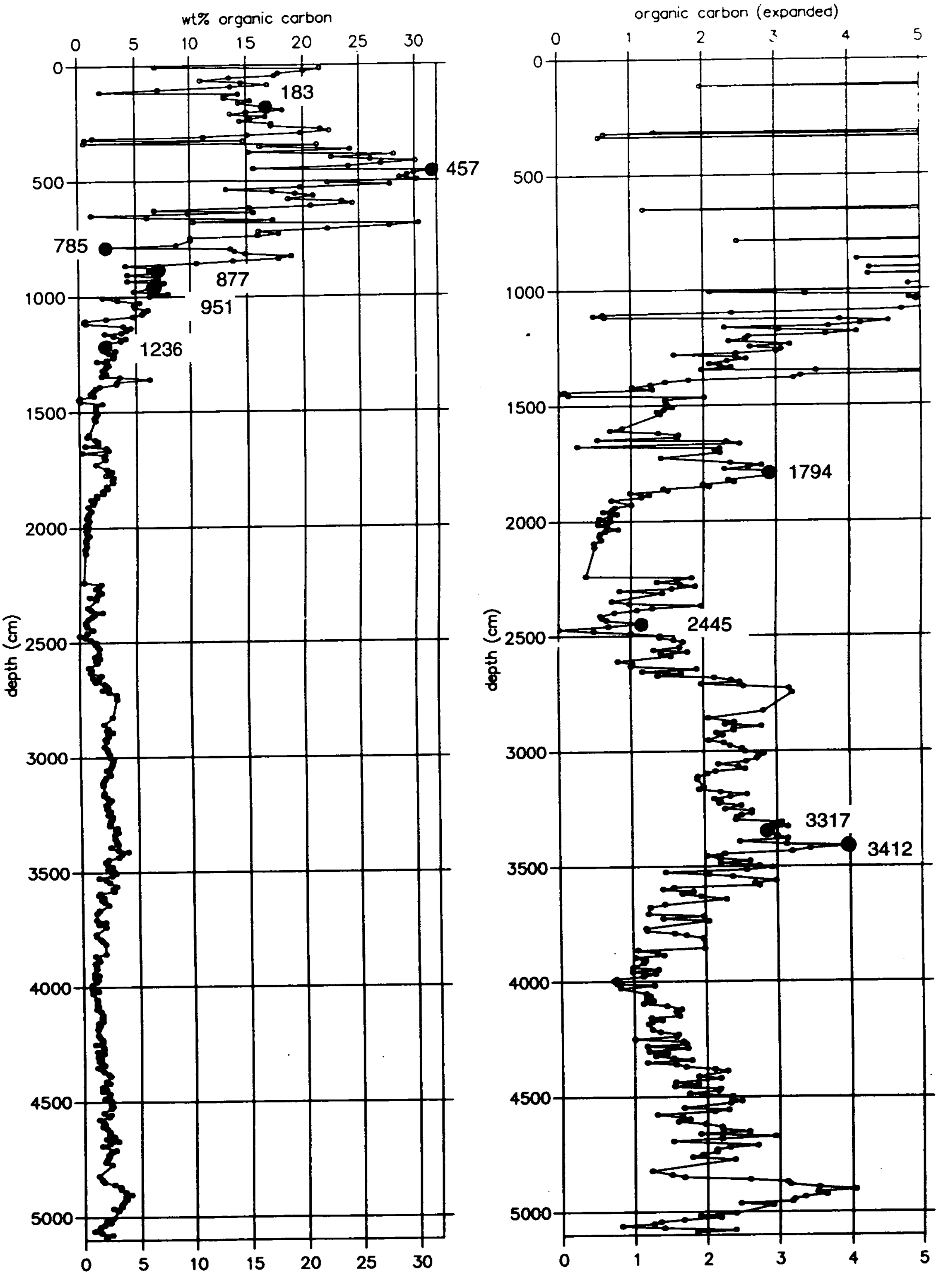


Fig. 5.2. Organic carbon content and samples selected for organic geochemistry

Ten samples were selected for organic geochemical analysis and their locations are shown in relation to the organic carbon profile in Fig. 5.2. These points are generally comparable to the sample points chosen for palynofacies examination, although a slightly different strategy was adopted. The procedures for extraction and determination of the alkane components are described in Appendix 1. Some basic parameters are shown for each sample in Table 5.3. and the n-alkane distributions are represented in Fig. 5.3 (as µg/g dry sediment).

The EOM content of the samples is broadly proportional to the organic carbon content (Table 5.3.) with r=0.983. The concentration of total extractable matter per gramme of organic carbon is shown by eomC. It can be seen that most samples have between 100 and 200mg of extractable organic matter (i.e. lipids) per gramme of organic carbon. However variations exist which must reflect the quality of organic matter in terms of its source components and/or degree of preservation (e.g. Wünsche et. al., 1987). The samples from the Holocene (183 and 457cm) and from 3317cm depth show the highest specific concentrations. This might reflect either higher contributions from (lipid-rich) planktoinic material or enhanced preservation of the lipid fraction. It is believed that lipids are more resistant to diagenetic removal than proteins and carbohydrates, but degrade more readily than kerogen (Ishiwatari and Ogura, 1984). It is not though that original proteins and carbohydrates are present in significant quantities after early burial and so preservation relative to kerogen may be the main diagenetic influence. There does not appear to be a simple downwards decrease in lipid content in the organic matter and this is another indicator of non steady state accumulation processes. It will be shown in over the next section that the main presence of alkanes is thought to be derived from higher plant material, such as leaf waxes. If this was extrapolated to the total lipid content, it may be the case that the high values for the Holocene and the sample at 3317cm reflect high contributions from terrestrial input together with some increased supply from planktonic matter in response to climatic amelioration and increased productivity. In turn, higher deposition rates of organic matter would have favoured preservation of the lipid components from microbial attack.

The carbon preference index (CPI) is a measure of the odd over even numbered dominance for n-alkane distributions. The dominance of odd numbered homologues such as C_{27}, C_{29} and C_{31} can be seen clearly in Fig. 5.3. CPI's were calculated according to Bray and Evans (1961) and range between 5 and 25. These high values are typical for immature organic matter containing a dominant contribution from primary higher plant and/or algal sources. Values up to 28 have been reported for contemporary vegetation in the Ellesmere region (Rieley et. al., 1991). In contrast, organic matter with a major contribution from bacterial alteration product n-alkanes would show a CPI value closer to 1 under most circumstances (Barnes and Barnes,

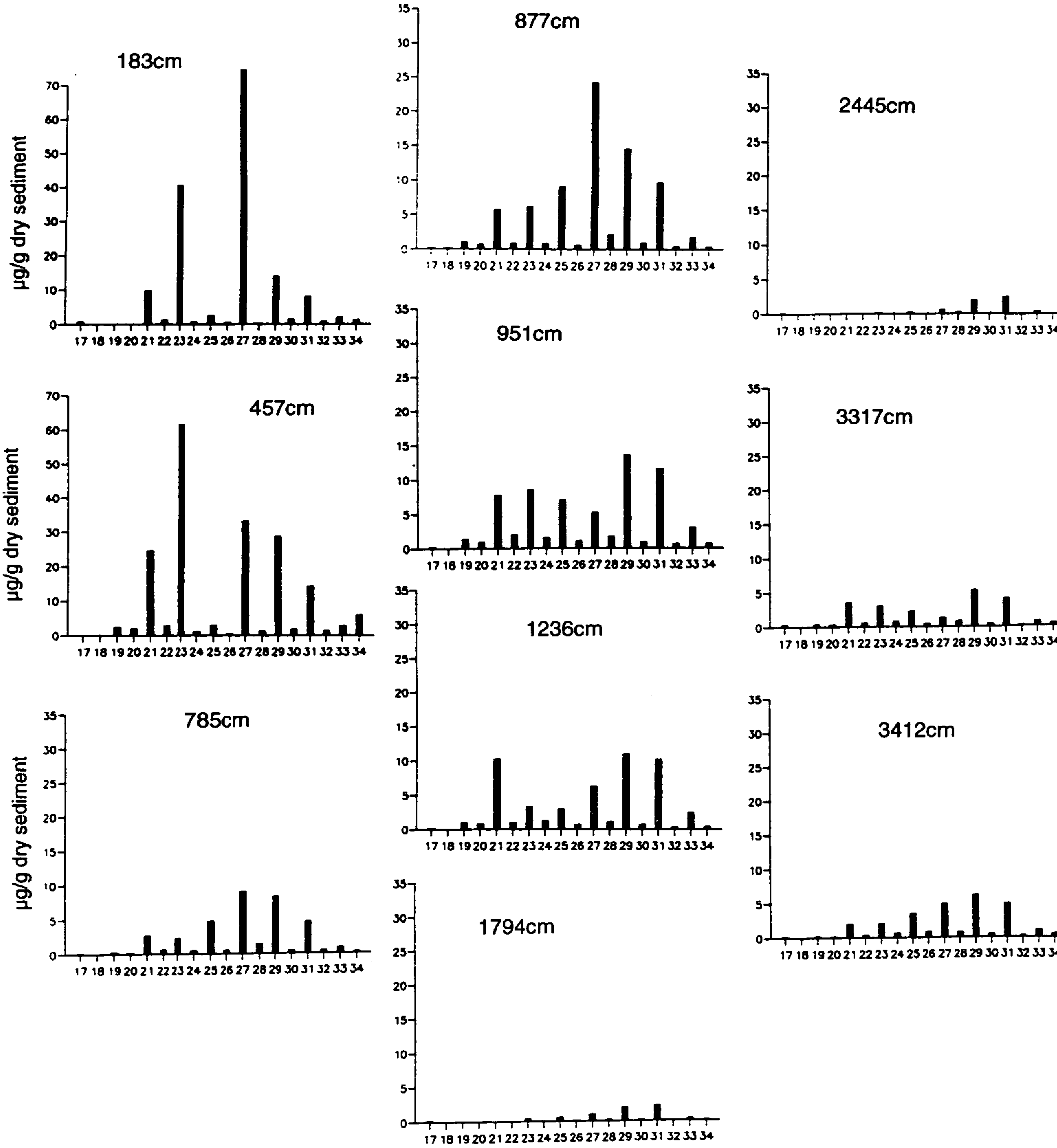

183cm
457cm
785cm
877cm
951cm
1236cm
1794cm
2445cm
3317cm
3412cm

Fig. 5.3. Distributions of n-alkanes in samples

1978). There appears to be some trend in CPI values in the profile, with the upper Holocene sample at 183cm showing the highest index and thus possibly the least bacterial reworking. Samples from lower in the profile typically show values of 10 or less, but the trend within these is not clear. The main point to note is the large difference between the sample at 183cm and those below. This may reflect more effective microbial reworking of the older samples either over an increased time period or more likely a change in the processes occurring in the uppermost zone of early diagenesis.

The n-alkane distributions (Fig. 5.3.) show the samples to be dominated by higher n-alkanes ($>C_{20}$) which probably reflect terrestrial plant contributions of wax, cutin and suberin. This conflicts somewhat with the pattern anticipated from C/N ratios and biogenic silica content values which would predict a bimodal distribution including an algal related maximum around C_{17} (Barnes and Barnes, 1978). It is most likely that the low abundance of shorter chain n-alkanes is related to their greater susceptibility to diagenetic removal. This has been shown in a number of studies where both sediments and living source matter (i.e. plants and aquatic organisms) have been analysed (Goossens et. al., 1989; Cranwell et. al., 1987). It seems that in many oxic and anoxic sedimentary environments the higher alkanes are less accessible to bacterial decomposers and so the sediments may under-represent the planktonic contribution. This prohibits the reliable use of ratios such as C_{17}/C_{27} which have been applied by some authors to assess the relative contribution of autochthonous versus allochthonous organic matter (Meyers et. al., 1984). It also contradicts earlier models suggesting that productive lakes should exhibit bimodal alkane distributions (Barnes and Barnes, 1978). It is possible that other classes of lipid planned for future analysis may reveal the contribution of algae more reliably. For example, algal-derived sterol compounds have been found to show a higher preservation potential than their alkane counterparts (Cranwell, 1988).

Amongst the higher alkanes, changes in patterns of dominance are found to occur. If it is assumed that the relative amounts of higher alkanes in the C_{23} to C_{33} range have not been altered by varying preservation potential (which may be reasonable), these patterns might reflect changes in higher plant source contributors. Firstly, if compounds $>C_{25}$ are examined it can be seen that the late Holocene sample at 183cm is dominated by C_{27} and this is also a major component in the three samples below. However, C_{29} is the dominant alkane in deeper samples (i.e. 951, 1236, 3317 and 3412cm). A third compound, C_{31}, forms a maximum in the samples at 1794 and 2445cm depth. These are the two samples with the lowest overall concentrations of n-alkane where no individual homologue exceeds 2µg/g in the sediment. A certain amount of data exists in the literature characterising living plants in terms of their n-alkane distributions. It is known, for example, that beech leaves are dominated by the C_{27} homologue (Rieley et. al., 1991). It might be possible that the sample at 183cm reflects a major contribution from the seasonal shedding of beech leaves, since beech is an abundant tree species in the present day catchment. Also, the C_{31} dominated samples at 1794 and 2445cm *might* reflect contributions from a more acidic or conifer influenced terrestrial vegetation as suggested by Cranwell (1990). However, the literature on individual plant and animal matter is still inadequate and regardless shows serious problems from overlap prohibiting simple relationships like this to be made securely. It is the case, for example, that many other trees bear a fingerprint with significant C_{27} presence. Further growth of the biochemical data base will be required to improve the potential for biomarker source correlation. Rieley et. al. (1991) advocate the use of a multivariate fitting technique using a wide range of measured compounds for matching purposes.

It is also evident from the distribution diagrams that certain samples contain a pronounced maximum centred on the C_{21} or C_{23} alkanes in addition to the maximum around C_{27} or C_{29}. This is most marked in the 457cm sample, although most of the other samples contain a relatively significant level of C_{21} and C_{23} compounds. It is not certain whether this represents a primary source contribution or not. Bacterial alteration products are known to lie in this range, but they typically possess significant even numbered distributions (Cranwell, 1990) and the samples observed here have a strong odd dominance. Most alkane distributions classically display a C_{17} peak for algae (if present in any quantity) and a peak *beyond* C_{25} for higher plants (e.g. Farr et. al., 1990). However, other aquatic plants (perhaps macrophytes) may display a peak in the C_{21} to C_{23} range (Barnes and Barnes, 1978). Investigations have shown that sphagnum moss contains a dominant signal from C_{21} and C_{23} alkanes (Corrigan et. al., 1973) and this may be the case for other mosses or lower plants growing at Monticchio. Not enough information is yet known to attribute these peaks to a particular source unequivocably.

In summary, the samples analysed show a maximum in the C_{25}-C_{33} range which is attributable to higher plant contributions and second maximum around C_{21}-C_{23} which as yet cannot be attributed with certainty. The latter is found in all the samples except perhaps that at 2445cm. None of the samples show a significant C_{17} peak attributable to algal sources.

In addition to straightforward n-alkanes, a number of other compounds were present in the aliphatic fraction analysed. Of particular importance appears to be a pair of compounds initially named as 'X' and 'Y' which are very abundant in samples 785, 877 and 951. These compounds are illustrated in Fig. 5.4. which shows a GC trace for the 877cm sample. Subsequent analysis by GC-MS determined that 'X' and 'Y' are monoenes (i.e. single unsaturated relatives) of 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane -a highly branched aliphatic compound. This has been previously documented by Rowland et. al. (1985) as

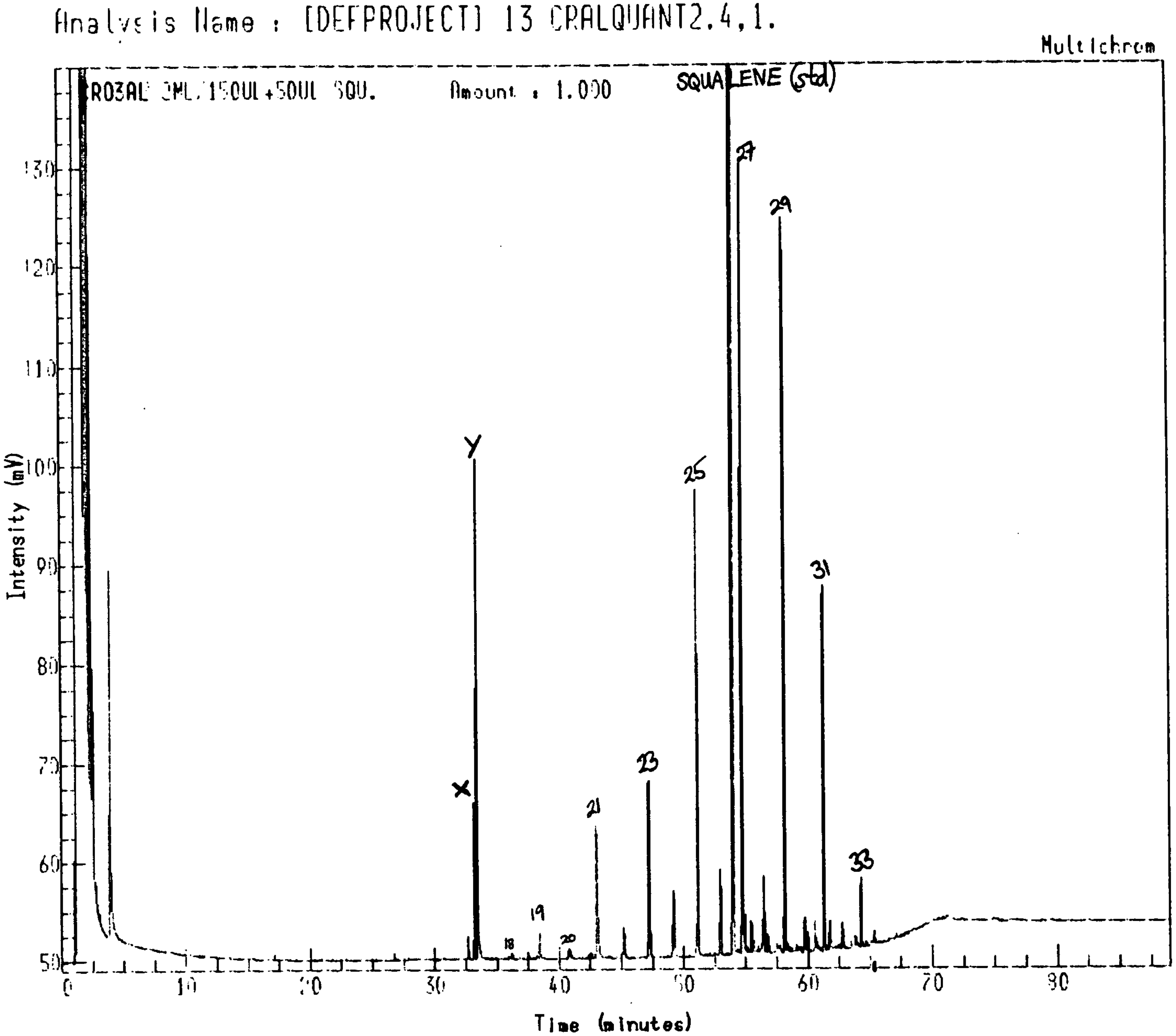


Fig. 5.4. GC trace of aliphatic fraction from 785cm sample (Note the predominance of odd-numbered higher n-alkanes (C_{21}-C_{33}) and the presence of X and Y)

occurring in certain green algae. It may therefore be the case that this is an indicator of a significant source contribution from algae. Branched chain compounds are perhaps more likely to survive bacterial degradation than their straight chain equivalents. At the moment its presence cannot be related to any specific contributor, although it is interesting to note its location dominantly in the 785 to 951cm area of this limited study.

CHAPTER 6

CONCLUDING REMARKS AND RELATIONSHIPS TO PALAEOENVIRONMENT

In the previous chapters the sediment geochemistry has been related to the possible influences of climate, volcanism, human effects and morphometric change in the lake system. This chapter will offer some concluding remarks on each of these influences, beginning with climate. At the end of the chapter the results anticipated from ongoing studies are summarised and some recommendations are made for further work.

CLIMATE

1) Long time scale changes

The main feature of the record over a long time scale is the presence of two broad cycles between <700 and 3400cm depth and between 3400 and 4900cm depth. These are shaped by changes between biogenic dominated and minerogenic dominated sediment zones. The changes have been described in Chaps. 4a and 4b and are restated by the profiles for Mg and organic carbon shown in Fig. 6.1. This overall pattern is considered to correspond strongly with the pollen record, such that biogenic dominated sediment zones are generally matched by maxima in arboreal or thermophilous pollen (c.f. Fig. 3.10.). These consistent trends which provide the major cycles in the Monticchio record are probably related to long term climatic variations. The trends are also summarised by multivariate evaluation of the chemical data (see Chap. 3) in terms of PC1 sample scores plotted against depth. This parameter will now be used as a proxy indicator of climate to illustrate possible correlations for the core with other well known climatic records. Such correlations permit ages to be inferred for the sediment record.

In Fig. 6.2. and Fig. 6.3. possible correlations are shown between the PC1 parameter and a detailed oxygen isotope record from the SW Indian Ocean (Martinson et. al., 1987). In Fig. 6.2. the older age model approach is taken while in Fig. 6.3. an attempt is made at a young age model fit. The correlation is made visually and is primarily based on fitting the major periods of climatic amelioraton (suggested by high PC1 values) to periods of low $\delta^{18}O$ value on the marine profile. This approach represents a somewhat subjective, but preliminary dating effort for the Monticchio profile using the geochemical record.

The older interpretation (Fig. 6.2.) is presently favoured, as has been discussed in preceding chapters. In this interpretation, the major peaks are thought to match well in the suggested stage 5 area. The earlier optimal period around 4900cm depth has been correlated with stage 7c, although it might alternatively represent stage 7a. The stage 7 period has been linked by some authors to the Holstein interglacial (Dansgaard et. al., 1993), but others have suggested that the Holstein is related to an earlier period such as isotope stage 9 or 11

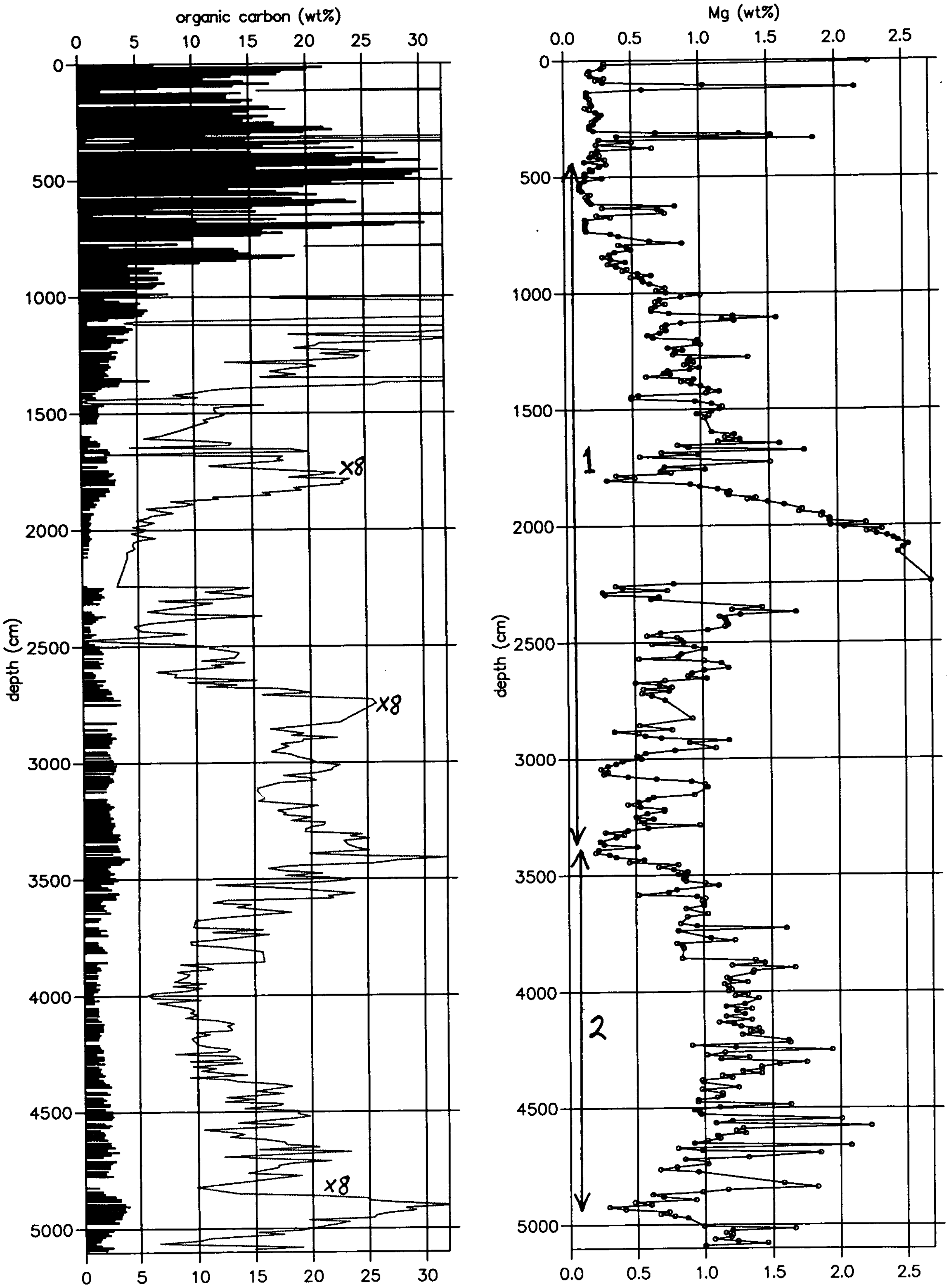


Fig. 6.1. Profiles for organic carbon (with additional x8 expansion line) and Mg (2 large scale cycles in sedimentation are marked)

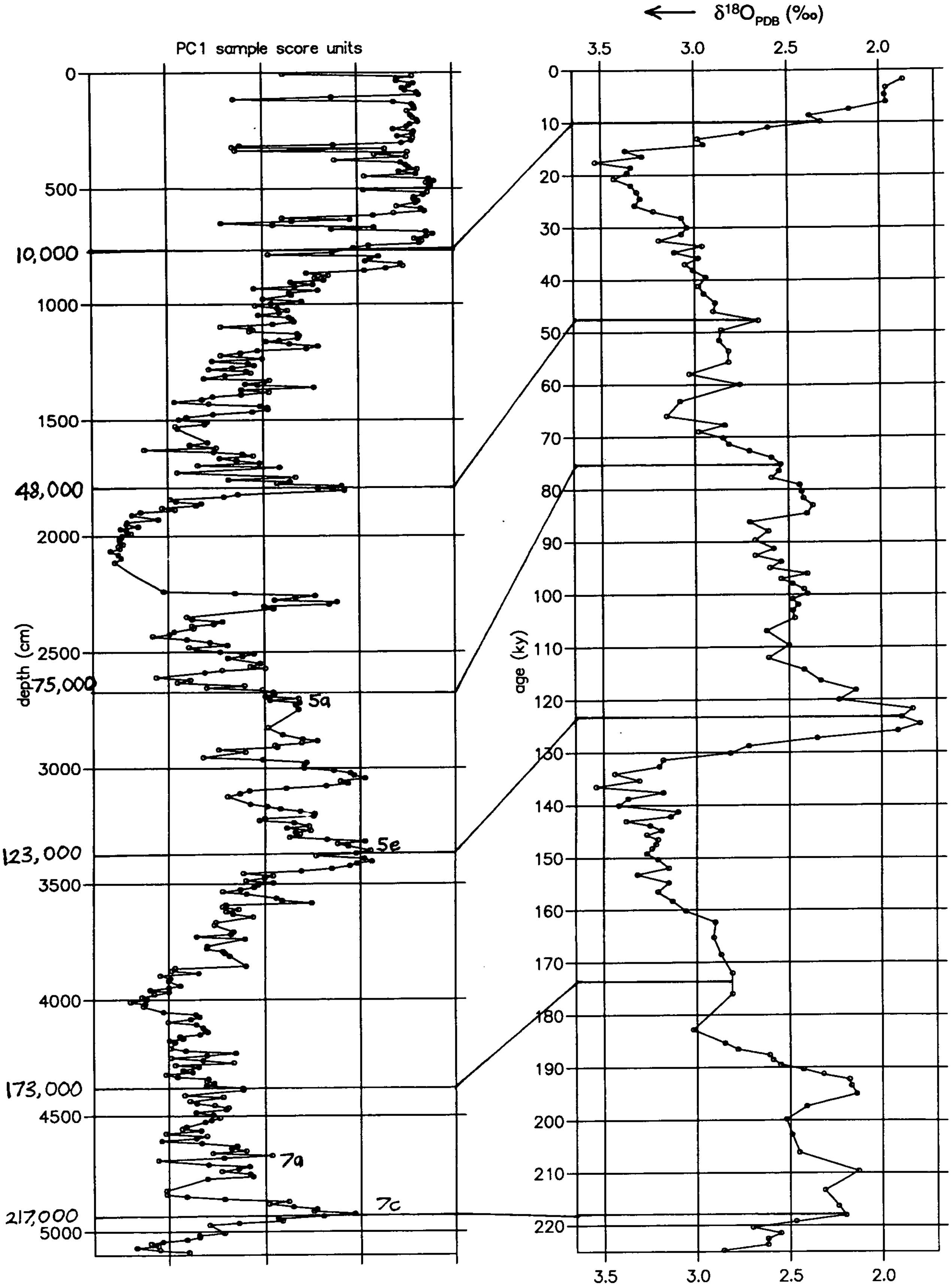


Fig. 6.2. Correlation between PC1 and an oxygen isotope record assuming an old age model (isotope record of planktonic foraminifera from SW Indian Ocean, Martinson et. al., 1987)

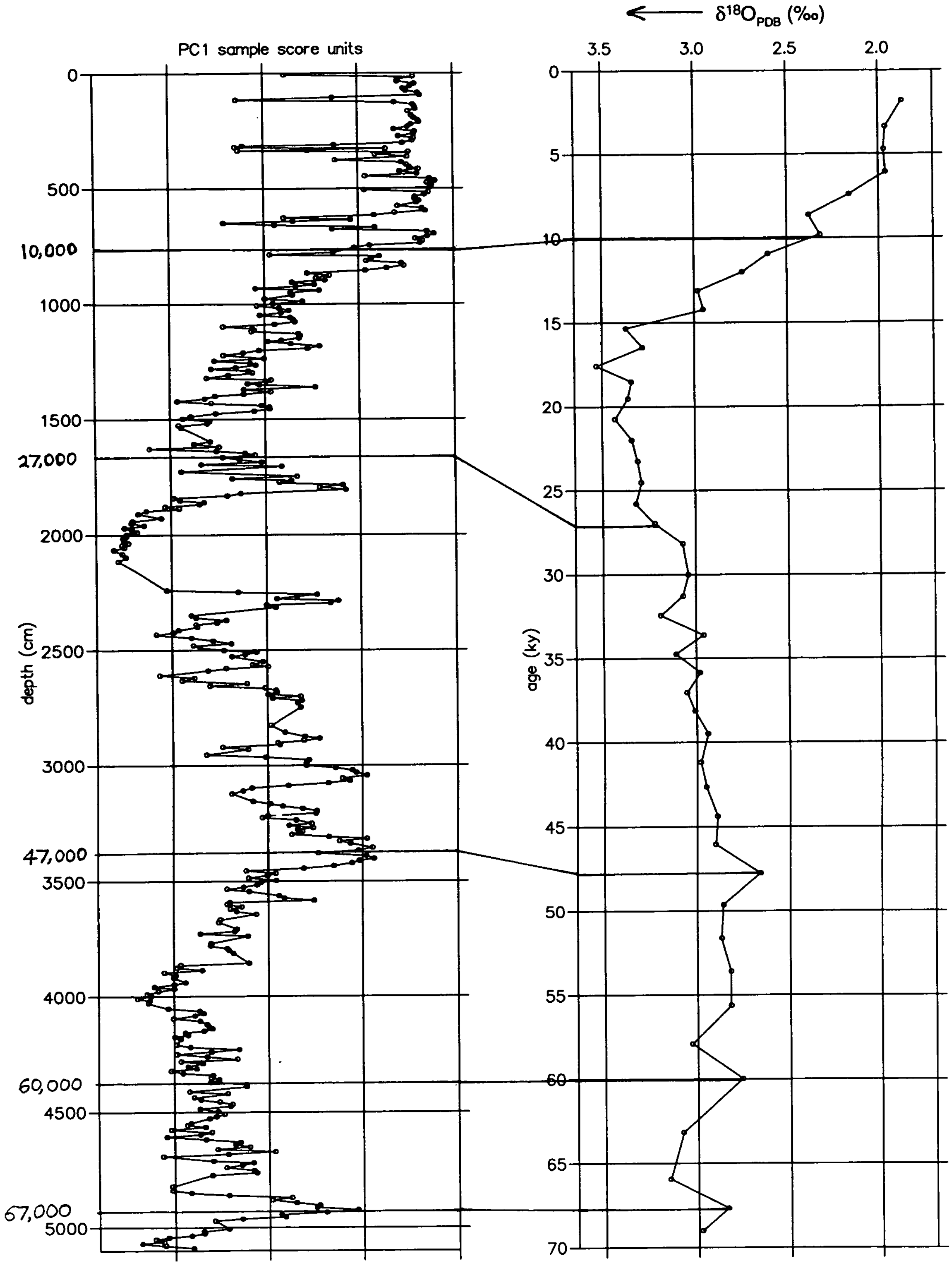


Fig. 6.3. Correlation between PC1 and an oxygen isotope record assuming a young age model (isotope record of planktonic foraminifera from SW Indian Ocean, Martinson et. al., 1987)

(Sarnthein et. al., 1986 and refs. therein). Regardless of the age for the Holstein, the base of the Monticchio record is here related to stage 7 and an approximate age of 225,000 years B.P. The alternative 'young' correlation suggested in Fig. 6.3. is considered to be weaker, although the marine isotopic curve illustrated represents just one possible record to correlate against. Visual attempts to correlate the young interpretation (i.e. a 60-70,000 year age for the base of the core) with other profiles such as the marine record of Heinrich events (Bond et. al., 1992) and the Greenland ice core record (Johnsen et. al., 1992) did not provide any obvious fit.

In adopting a 225,000 year age model for Monticchio a fundamental difficulty is recognised: the need to account for the reduced magnitude of the Eemian and stage 7 interglacial signals in comparison with the Holocene. If anything, the Eemian may have been some 2-4°C warmer and also moister than the Holocene (Guiot et. al., 1989; Dansgaard and Duplessey, 1981). The evidence from both sediment geochemistry reflecting biogenic productivity in the lake system and from pollen reflecting more directly climate as experienced by the surrounding terrestrial environment shows peaks of lesser magnitude at 3400 and at 4900cm. It might be reasonable to explain the former as a reflection of the idiosyncrasies often found in the local environment of a lake system. However, the pollen record is more difficult to explain since *most* pollen records are believed to reflect climate reliably and differences between the Holocene and Eemian are not found like in this situation. Typically, other documented long pollen records from the region show peaks in arboreal and thermophilous taxa during the Eemian that are as high or higher than during the Holocene (van der Hammen et. al., 1971; Pons et. al., 1992; Follieri et. al., 1993; 1988; Francus et. al., 1993).

The fundamental control on the biogenic content of the sediments (or productivity) was suggested to be nutrient levels (Chap. 4a). This may be regulated through leaching of macro-nutrients such as P and other components from the catchment soil-weathering system. The model for interglacial to glacial changes in maar productivity which involves a changing vegetation cover (Truze, 1990) has already been mentioned. It is thought that climate (particularly available moisture) has a dominant and underlying influence on this whole process by regulating the vegetation development and the amount of water movement through the catchment weathering zone. Increased vegetation cover and soil moisture may cause a build up of soil organic matter and acidity encouraging leaching (Duchaufour, 1982). Such processes might be loosely connected to the theories developed in Scandinavia by Iversen (1958) and Andersen (1966).

The Scandinavian approach included division of the glacial-interglacial cycle into four phases (Fig. 6.4.). Solifluction and periglacial processes were thought to remove soil and provide a fresh base-rich substrate for colonisation once climate improved during an interglacial. As vegetation developed on this soil it progressively changed the composition through removal of components, chemical differentiation and the input of organic compounds. This led to a decline in soil fertility during the later stages of the glacial. This was a time when climate was also deteriorating, but the change in soil was considered to be independent of that in climate.

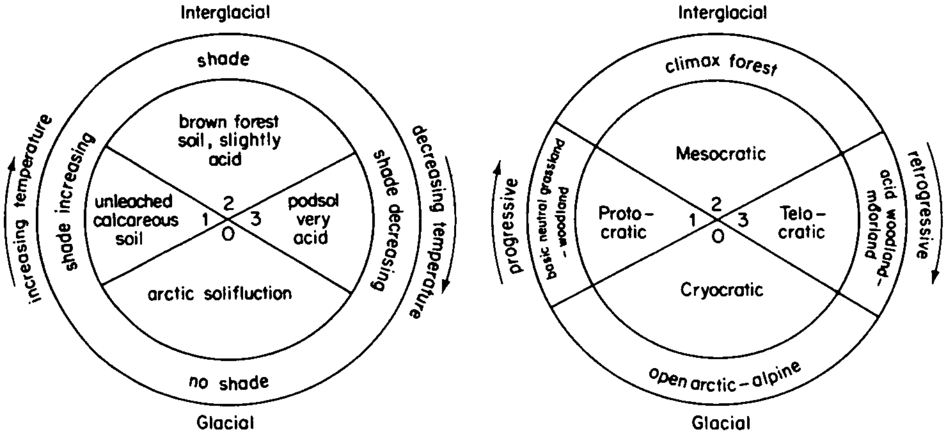


Fig. 6.4. Iversen based theory of glacial-interglacial cycles
(from van der Hammen et. al., 1971)

In a Mediterranean lake catchment it may not be likely that solifluction processes operated in a comparable way to the high latitude periglacial zones (Birks, 1986). To remove old (acidified?) soil layers and provide a fresh inorganic starting material would normally require an adequate level of catchment erosion during the glacial. If the rate of erosion was low, little new base-rich mineral matter would become available. On the other hand, external supply from tephra falls or local disturbances (seismic or eruptive) could alter the balance in place of solifluction. This has been suggested as a possible mechanism in Chaps. 4a and 4b.

An alternative control on sedimentation (i.e. depositional facies) by changing lake levels has been reconstructed in some studies (Street and Grove, 1976; 1979; Lamb et. al., 1989; Harrison et. al., 1991). Such reconstructions are often compiled from multiple sites to produce a regional palaeohydrological and henceforth climatic record. Lakes in Africa have been particularly amenable to this approach due to their often strong changes in water balance and regional drops have been interpreted in terms of arid climatic periods. No concrete evidence appears to be available for strong lake level fluctuations in the 1990 Monticchio core. It *may* be the case that the groundwater reservoir has always remained relatively stable with no great rises or falls in level. It is to be expected that the shelf location cored would not represent the most **sensitive** site to record such changes in lake level, and that perhaps nearshore sediment cores would reveal more evidence. The presence of moss layers which may not be in situ, and of high level terraces provide only speculative evidence at present (Chap. 2). It has been suggested that the $\delta^{18}O$ changes in calcite precipitated between 1900 and 1600cm in the sediment record may indicate a period of decreasing water balance, but more sampling is required in this area (Chap. 4c). A nearshore core together with more detailed geomorphological fieldwork might provide better indications of lake level changes. Thus the main arguments for changing sediment geochemistry in this discussion have concentrated on the changing catchment soil and vegetational regime.

In attempting to explain the difference between the Holocene and earlier interglacial signals five possible factors are suggested:

1) climate was different during the Eemian (less available moisture?)
2) the pollen record is not representative of the vegetation in a consistent way
3) soils have changed due to the long term evolution of vegetational systems and through the effects of tephra blanketing and perhaps earthquake/local eruptive disturbance
4) the lake has gone through a succession towards increased trophic status and biogenic dominated sedimentation associated with gradual infilling
5) local hydrology has changed (towards a moister soil regime) during the disturbance associated with turbidite deposition

Of these factors the first is a regional or global effect while the rest are more local in nature. It is not thought that the first possiblity is likely (as discussed above) since evidence from other sites does not support the existence of a poorer climate during the last interglacial. Pollen might show unrepresentative behaviour if for example selective preservation of certain genera took place during the Eemian or an irregular pattern of pollen distribution or reworking occurred. None of these processes appear immediately obvious from the palynological work (B. Huntley, pers. comm.).

The third and fourth factors have already been proposed in Chaps. 4a and 4b as an explanation for the sediment geochemistry. The soil change hypothesis is also offered as an explanation for the pollen record. This may be debatable since arboreal vegetation might be capable of reaching adequate nutrient and moisture reservoirs through deep root systems and might not suffer from surficial degraded soil layers. It may be the case that chemical differentiation establishes a recyclable nutrient-rich layer below the surface which could sustain arboreal vegetation indefinitely and therefore only climate (in particular available moisture) would be an influential factor. Nevertheless, the Scandinavian theories discussed previously show that soils may become depleted through long periods of vegetation cover, leading to a deterioration in the quality of vegetation. This would need to be a local effect, however, since other sites in the region do not show indications of a similar process (B. Huntley, pers. comm.).

Hydrological change might lead to a moister regime in the catchment soil zone and thus encourage vegetation growth and nutrient leaching. This sort of change has been envoked in the case of Lago di Monterosi where construction of a Roman road caused a major redirection of spring systems into the lake (Moss, 1988; Hutchinson, 1970). It is possible that a major tectonic disturbance such as an earthquake or phreatomagmatic eruption event could cause such a shift. However, this is speculative and difficult to prove. It remains as a possibility which is not easily tested.

If it is assumed that an old age model is correct for the Monticchio record, this interpretation might be extended to estimate the sediment accumulation rates for some broad time windows (Table 6.1.).

depth interval	mean sed. rate	time window (years)
1) 0-750cm	0.75mm/year	(0-10,000)
2) 750-1800cm	0.27mm/year	(10,000-48,000)
3) 1800-2700cm	0.33mm/year	(48,000-75,000)
4) 2700-3350cm	0.13mm/year	(75,000-123,000)
5) 3350-4350cm	0.20mm/year	(123,000-173,000)
6) 4350-4900cm	0.12mm/year	(173,000-217,000)
7) 4900-5100cm	0.25mm/year	(217,000-225,000)

Table 6.1. Estimated mean linear sedimentation rates for selected time windows based on the assumption of an old age model.

These figures show a high accumulation rate for the Holocene sediment record which has already been described as an uncompacted zone associated with high contributions of autochthonous biogenic matter (Chaps. 3 and 4a). In contrast, accumulation rates some 3-6 times lower are found for the other parts of the core. Although biogenic productivity may be responsible for the difference between the Holocene and earlier sediments, it may be the case that clastic erosion is more important in regulating the differences within the earlier parts of the core. Clastic deposition is obviously the dominant factor in the case of tephra and turbidite depositional events. It will require objective sedimentation rate data to evaluate the long term influences of autochthonous productivity versus clastic erosion in controlling these rates for the lower zones. It should be noted that the mean rate of 0.33mm/year for the zone between 1800 and 2700cm includes the turbidite sequence where occasional rates of 1mm/year or even 10mm/year may have existed (Zolitschka and Negendank, in prep.). Therefore the normal fine grained sediments in this zone are probably associated with accumulation rates closer to 0.2mm/year or less.

Relationship with generally accepted climate models for S. Europe

The general climatic model for low to middle elevation S. Europe during the glacial period is one of a cool and semi-arid steppe environment dominated by sage brush, grasses and weeds. This was reconstructed by early pollen studies (e.g. Bonatti, 1966) and for a time superceded a previous theory of pluvial conditions during the glacial period. It was suggested that a cooler N Atlantic provided less evaporative moisture pick up for the wind belts and consequently less rainfall.

Later evidence from N Mediterranean sites supported the idea of a semi-arid and treeless vegetation type (Bertolani-Marchetti, 1985), but it was also recognised that higher rainfall totals and higher lake levels may have existed during the glacial period (e.g. Giraudi, 1989). These observations are reconciled if the majority of rainfall occurs during the winter months i.e. outside the crucial growing season for plants (Prentice et. al., 1992). In this situation, enhanced total rainfall providing high surface runoff can exist in conjunction with an arid flora because of the cool dry summer season. The higher winter rainfall totals might be governed by increased storm frequency under a southward shifted and intensified jet stream.

This pattern may be typical for the Mediterranean region and for high latitude deserts in other parts of the world (Spaulding, 1991). It contrasts with a belt further to the south (e.g. most of N Africa) which experienced pluvial conditions during optimal interglacial periods. This latter zone may reflect the poleward displacement of the summer monsoon system during the interglacial and is marked by a strong summer seasonality of precipitation.

In summary, Lago Grande di Monticchio is predicted to have experienced markedly drier and perhaps cooler summers during the glacial period and winters which were wetter and substantially cooler. Rossignol-Strick et. al. (1992) suggest that at low to middle elevations both temperature and rainfall have an influence on vegetation dynamics in the Italian region, but that rainfall is the more critical. The result of a steppe vegetation cover would influence the lake sedimentation through perhaps a reduction in leaching activity and consequently nutrient inputs to the lake. The glacial environment may also have experienced sporadic periods of increased erosion associated with higher winter rainfall. If the overall water balance during the glacial was not much lower than at present, this would explain the absence of severe lake level drops or desiccation features in the sediment record. It might be the case that the lake level was actually higher than during the Holocene.

2) 1000 to 10,000 year patterns of change

A number of shorter duration variations are seen in profiles such as PC1 or organic carbon content (and also in the pollen record). These may be related to minor climatic oscillations such as stadial-interstadial events. One particular example is indicated by the marked increase in organic carbon content between 1340 and 1390cm depth (see Fig. 4.2.). This may represent a period of up to 2000 years extent, although independent dating and more detailed pollen coverage would be useful before further interpretation is made. There are also significant peaks at 1800cm and 2300cm separated by the turbidite zone, and a peak at 2550cm depth. These either represent limited regional oscillations (possibly influenced by the sensitivity of the particular site) or changes which can be correlated over long distances.

Attempts were made to correlate the record between 750 and 1800cm (which might represent the time interval from 10,000 to 48,000 years B.P.) with data from the polar ice core records (Johnsen et. al., 1992) and from Heinrich event records in the NW Atlantic Ocean (Bond et. al., 1992). Neither of these comparisons could be seen to match and it was concluded that no firm or visually obvious correlations exist between these shorter term oscillations and trends in the geochemical record. An illustration of this is provided by Fig. 6.5. which shows how the more recent Younger Dryas and Bølling-Allerød periods might correlate between PC1 and the Greenland ice record, but shows the absence of a clear match in the 14,000 to 40,000 years range. Neither was any reasonable match possible with these records on a younger age model basis. (This incorporated the periods of climatic amelioration at 2700, 3050 and 3400cm as reflecting interstadials of <50,000 years age.)

It would be easy to conclude from this that the finer oscillations seen in different global records are local phenomena rather than widespread features. This has been argued for to some extent by Behre (1989), Kukla (1989) and Broecker et. al. (1988). On the other hand the dating controls are presently not adequate both for the ice and marine records and more so for the Monticchio record to attempt such links and to imply their genetic relationships.

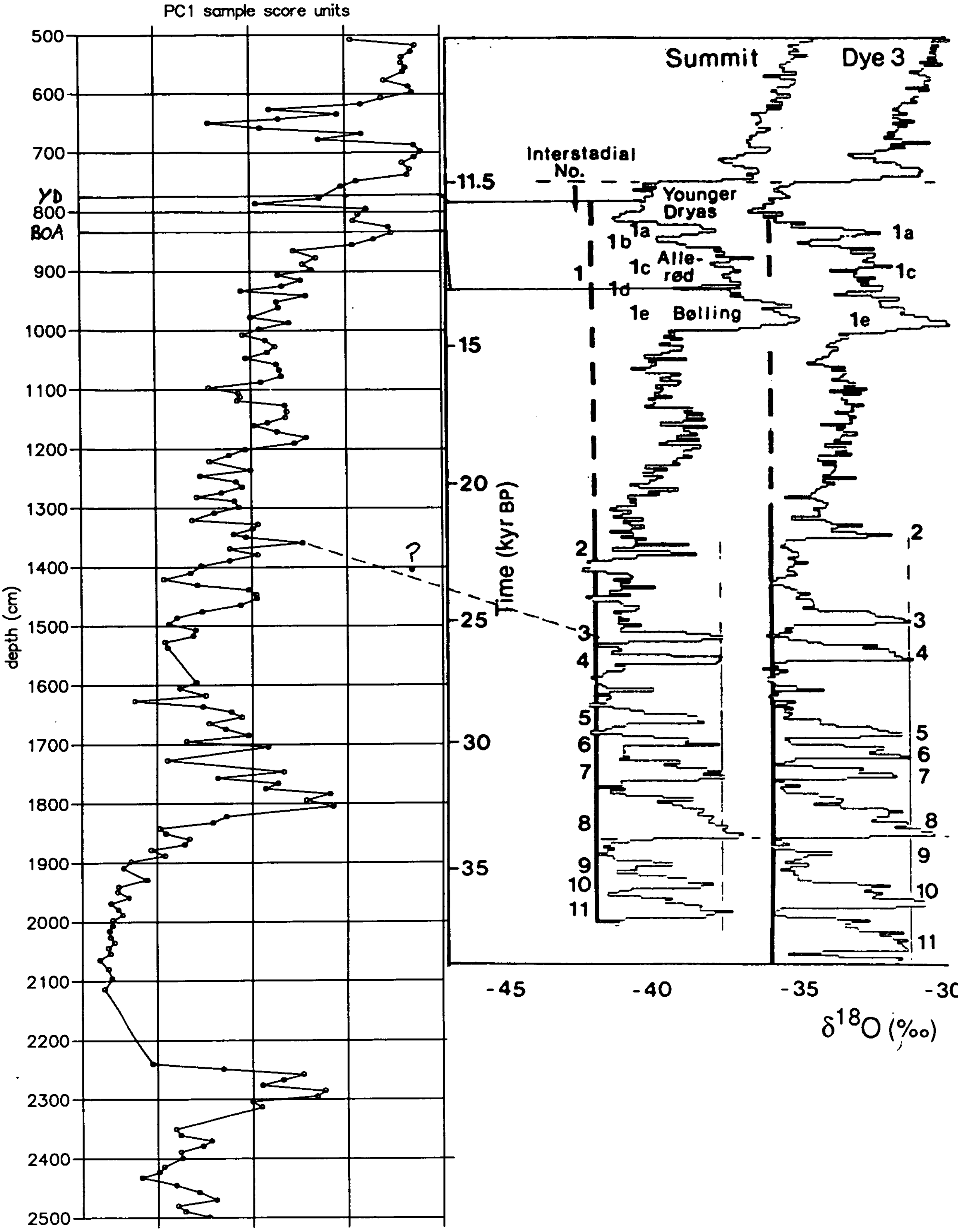


Fig. 6.5. Comparison of PC1 between 1500 and 2500cm depth with oxygen isotope records from the Greenland ice sheet (Johnsen et. al, 1992)

3) Younger Dryas period

The presence of the Younger Dryas in the Italian region has recently been highlighted by palynological evidence (Lowe, 1992; Rossignol-Strick and Planchais, 1989). This follows earlier work which suggested that the Mediterranean may not have responded sensitively to such an event (e.g. Bertolani-Marchetti, 1985).

It appears that the Younger Dryas may well be present in the geochemical record at 750 to 800cm depth and therefore that Lago Grande di Monticchio has been sensitive towards what is known to be an abrupt climatic change (Berger and Labeyrie, 1987). As a reminder, some trends in the geochemistry across this zone are compiled in Fig. 6.6. The main features of this interval appear to be a sharp drop in terrestrial organic matter as evidenced by organic carbon and C/N ratio decreases and a corresponding rise in the relative amount of lithogenic components such as Al. This may reflect a simple dilution-enhancement or perhaps a real rise in the rate of mineral erosion. The geochemical changes may be driven by a climate induced decrease in catchment vegetation cover and its secondary effects. More information will become available when varve counting and detailed pollen examination across this zone have been completed. It will probably be difficult to acquire accurate radiocarbon ages for this period due to the problems discussed in Chap. 3.

4) The Holocene period

The main features of the Holocene are the decrease in organic carbon content in the upper 500cm as compared to the early Holocene/post-glacial zone at 500 to 850cm depth and the concentration of diagenetic phases (in particular vivianite) in the early Holocene zone. This contrasts with the upper 400 or 500cm where diagenetic Fe phases appear to be virtually absent. These changes are thought to reflect either:

1) impoverishment of the catchment soils by one way leaching removal of nutrients, Fe, Mn and bases
2) human interference such as clearance upsetting the sedimentation regime

The second alternative does not bear substantial supporting evidence *so far.* No abrupt rises in pollen indicators such as vine or walnut which might indicate Neolithic/Bronze Age cultivation activity and clearance have been found in the record around 500cm and there is no other archaeological evidence available for increased cultural activity. The first explanation is considered possible and has already been envoked in the interpretation of vivianite occurrence (Chap. 4c). This process might be similar to Iversen's protocratic to mesocratic succession (Fig. 6.4.) already discussed for the longer time scale changes. In this

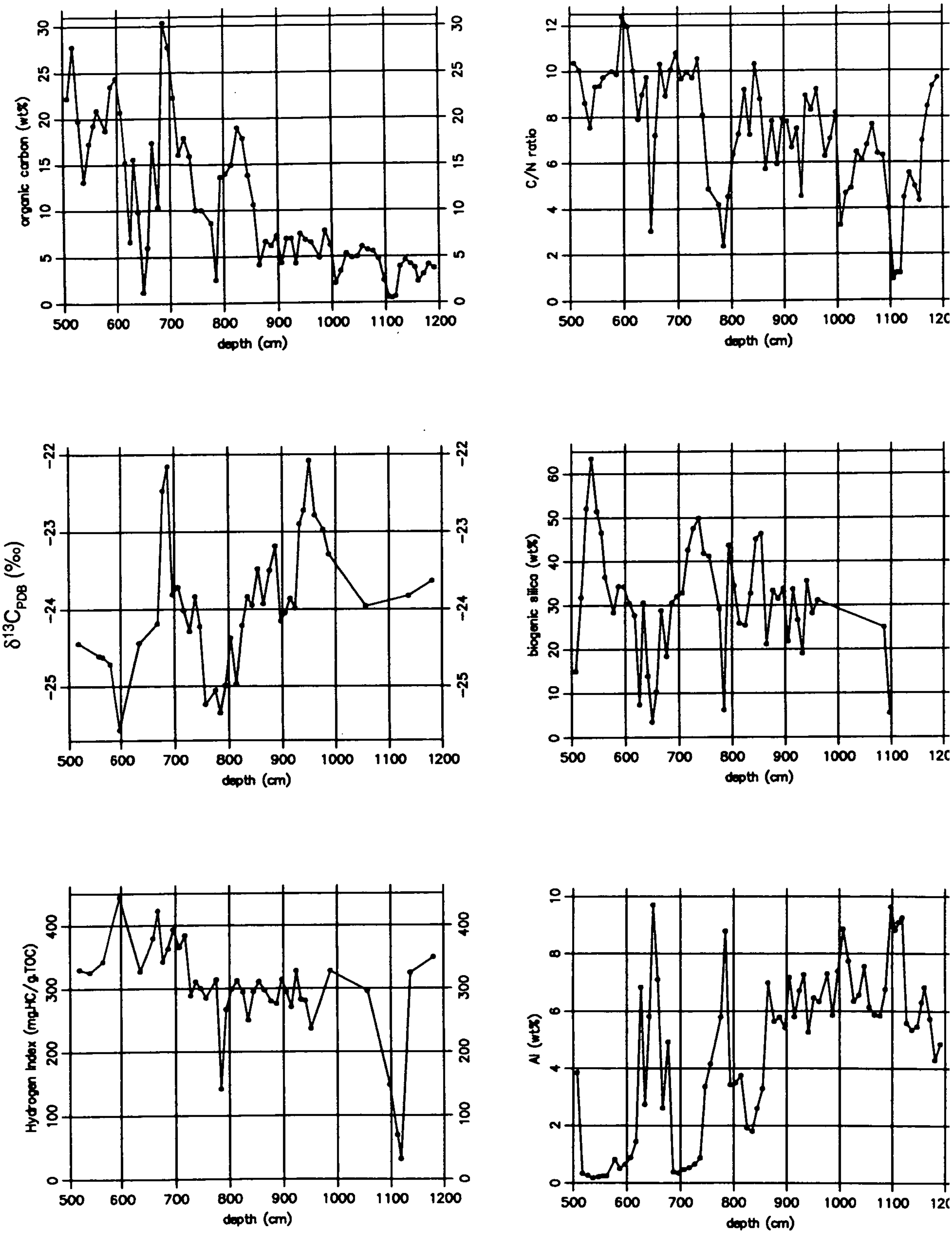


Fig. 6.6. Examination of a possible Younger Dryas signature seen in the Monticchio record between 750 and 800cm depth

case, over a period of 10,000 years in which the Monticchio catchment has probably seen a forest vegetation cover (Watts, 1985), the soil system may have been depleted sufficiently to provide lower input levels of key nutrients to the lake. Other components such as Fe may also have been depleted. Extrapolation of this process would predict an even lower productive state and supply of metals over the next 10,000 years (all other things being equal). However this will probably have been offset by anthropogenic pollution during the last few decades distorting the limnological system. There exists a good possibility of reconstructing the Holocene period at an annual resolution following varve analysis that is in progress (Zolitshcka and Negendank, in prep.).

VOLCANISM (tephra)

The impact of tephra contributions has been described in Chaps. 4a and 4b. The relationship between a histogram of tephra thickness per unit depth and PC2 (see Chap. 3) reflecting samples rich in tephra material is clear from Fig. 6.7. This study highlights the influence of the tephra on the sediment geochemistry of the Monticchio profile. The influence of tephra input and its secondary effects from blanketing the catchment are becoming increasingly recognised in parts of the world such as Iceland where volcanic activity has been prevalent during the last few thousand years (Einarsson et. al., 1993). The situation here may represent similar processes over a longer time scale during which the independent factor of climatic change has played a key role in shaping the sediments too. The apparent peaks in activity during the upper 1700cm (40,000 years?) of the record and locally in deeper regions of the core (such as at 3850cm) are thought to have regional implications for volcanism, but this is another study in itself. There is scope for much further work to be done by the groups at Edinburgh and Rome in characterising this detailed record of eruptions.

With the 10cm sampling resolution adopted it is not possible to accurately evaluate the extent of secondary inwash from the tephra fall events. This has been modelled by some workers as an exponentially decreasing content of ash above the visible tephra layer (Thompson et. al., 1986). It would appear that the samples immediately adjacent to most tephra layers return to background sedimentation levels rapidly. This is illustrated in Fig. 6.8. by the short duration of Al peaks and their return to 'base level' within 10 or 20cm. In such cases it is possible to estimate the length of catchment recovery time (from the mean sedimentation rates in Table 6.1.) as being typically no more than 500 years and perhaps much less than this. Of course, this is only a crude measure of the decline in secondary catchment material washed into the lake. It has been suggested in this thesis that the effects from weathering or leaching of catchment bound tephra over a *longer* time scale could be

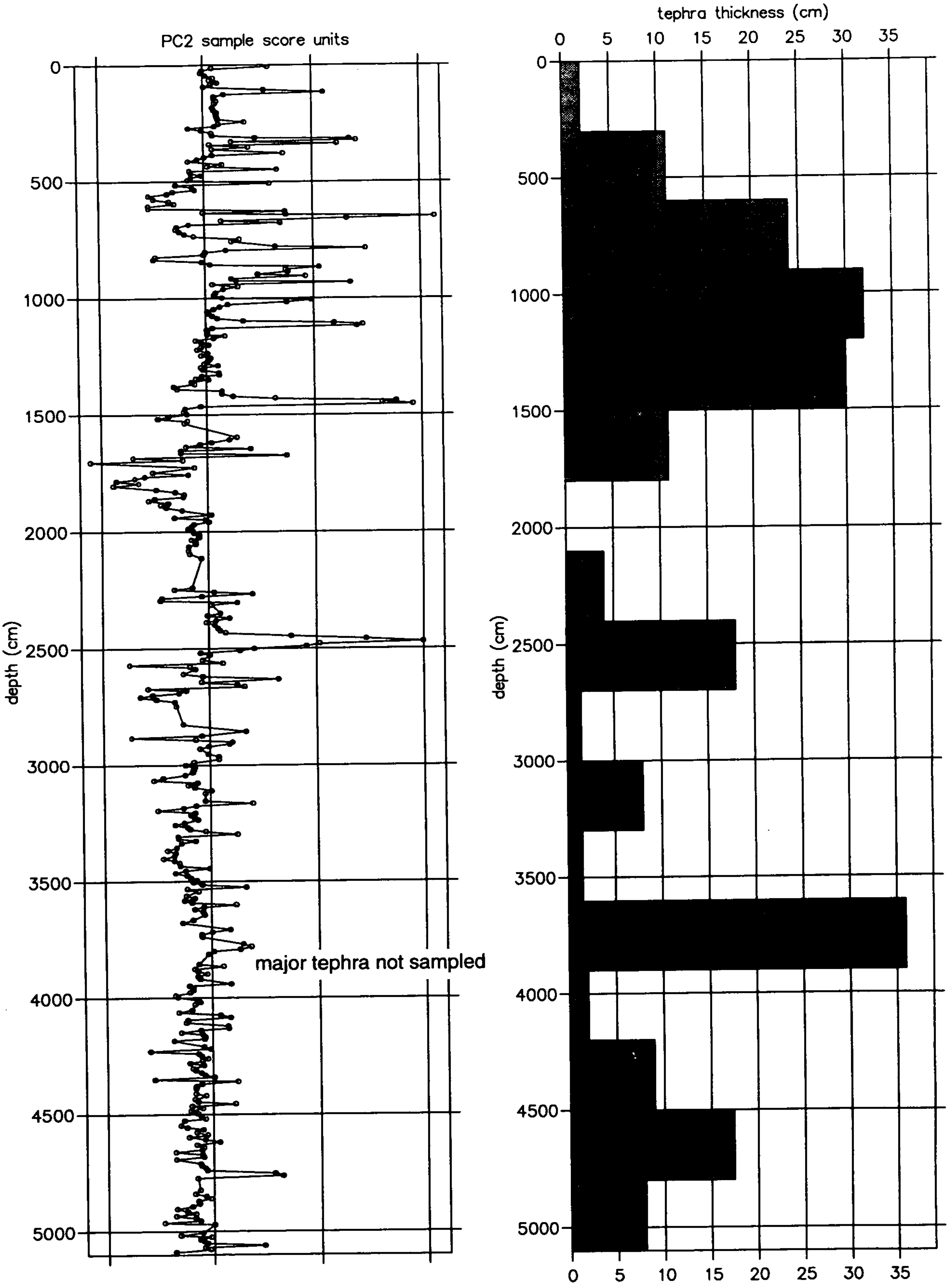


Fig. 6.7. Comparison of PC2 with tephra thickness

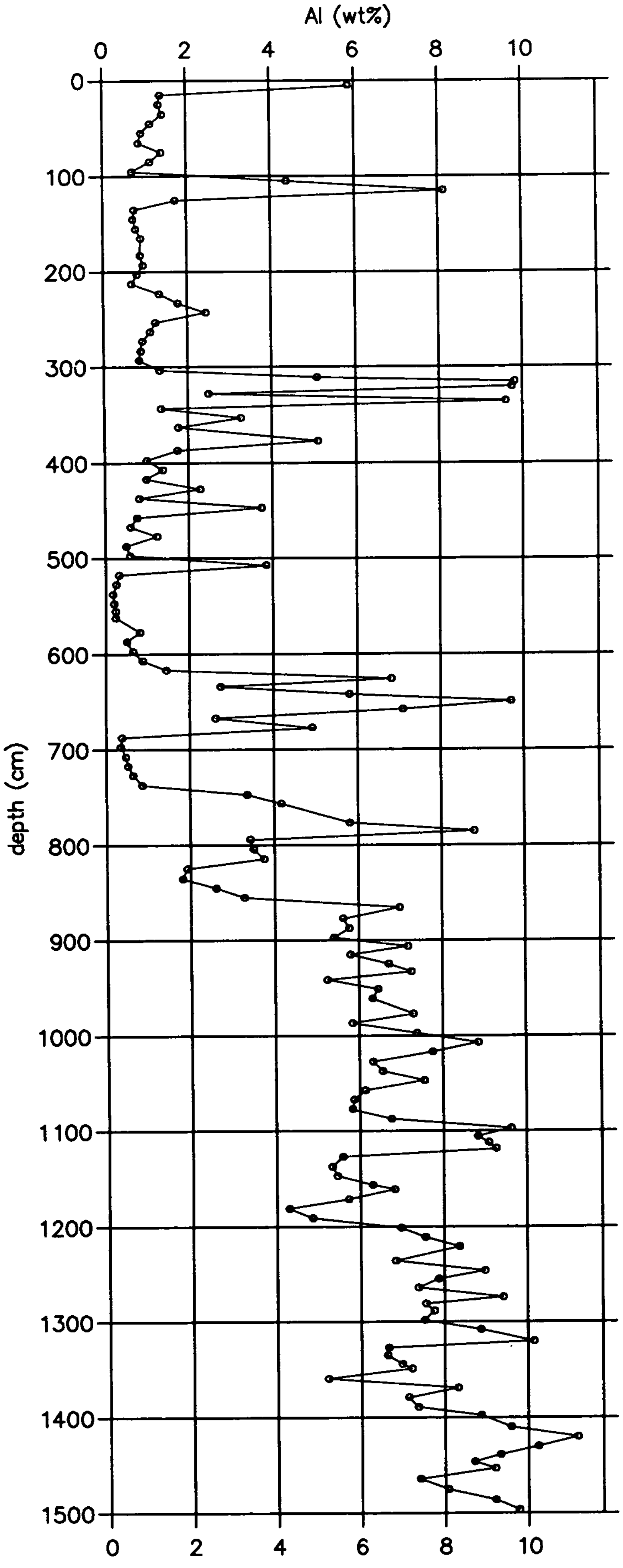


Fig. 6.8. Al content as an indicator of tephra deposition in the upper 1500cm

very significant. It is probably impossible to reconstruct how important the tephra factor was towards causing productivity changes. Only a quantitative suggestion that this has been a significant process is stated.

MORPHOMETRIC EVOLUTION

Lago Grande di Monticchio is essentially a shallow (<12m deep) lake at present, although a localised deep pit occurs. In perspective this probably represents a late stage in the lake's evolutionary history. It is known for maar lakes of comparable surface area to have water depths of 60 metres or more during a less filled stage (Negendank and Zolitschka, 1993b). Perhaps the water depth at Monticchio was considerably greater than 60 metres initially. A natural succession may have taken place towards more biogenic dominated sediments which are often associated with the late stages in a lake's ontogeny (Moss, 1988). Perhaps a gradual infilling has occurred in the absence of strong lake level changes. The rate of this shallowing process may be difficult to evaluate independently, although it would be interesting to see how results from diatom analysis fitted in with the sediment history. If the present sediment accumulation rate continues it would appear likely that the lake will emerge into a mire within 20,000 years or so. Plans to dredge the uppermost sediments (Stefanon, 1993) would of course delay this progression. Further fieldwork is necessary to understand the significance of the deep cauldron feature in relation to the overall setting.

HUMAN EFFECTS

The upper 300cm have been suggested as reflecting approximately the last 4000 years with the top few centuries of sediment record known to be missing (Chap. 4c). In this part of the profile trace metal enrichments are observed and tentatively related to Bronze Age or Roman cultural activity (Chap. 4c). Further work is required if the significance of these effects is to be interpreted in more detail. With the exception of artificial drainage and lowering, it might be reasonable to conclude that human activity does not appear to have caused any *dramatic* changes in the Monticchio catchment as has been the case for certain other lakes. For example, in Lago di Monterosi the construction of a road during Roman times caused profound increases in sedimentation rate and productivity for a period of approximately 500 years afterwards (Moss, 1988; Hutchinson, 1970). Recent tourism may be responsible for a current intensification of disturbance through sewage inputs. The current lack of available documentation for events prior to the Middle Ages and of a detailed sediment chronology makes it difficult to reconstruct what are possibly subtle changes caused by man.

RESULTS ANTICIPATED

1) Ar-Ar dates from four tephra layers between 1100 and 3850cm depth. This *may* provide the much needed objective data to answer the main age interpretation problem.
2) varve thin section analysis over the next two years should provide complimentary details on the make up of the sediments and estimates of sedimentation rates and sedimentary processes in general. Archaeological information might be deduced from the presence of charcoal particles.
3) ongoing organic geochemical work will provide an unusually detailed account of the organic matter composition from a long lacustrine record. GC-IRMS work may eliminate some of the possible explanations for the variaition of stable carbon isotopic ratios in the organic matter and lead to a better understanding of the local and/or regional significance of this isotopic parameter.

FURTHER WORK

1) more bulk radiocarbon dates would be desirable, perhaps a sequence of half a dozen samples in an attempt to recover some indication of sedimentation rates. Obviously the carbon dating work requires the commitment of significant resources and any bulk dates obtained would provide imperfect data to evaluate (see Chap. 3). Macrofossil a.m.s. dating of bryophyte samples should be avoided, although dating of birch fruits might be attempted. Although not 100% secure, birch fruits should possess a lower risk of reworking (B. Huntley, pers. comm.).
2) soil studies in the catchment including core profiles down to the primary volcanic material below. This should reveal whether the soils are thick and multilayered (e.g. influenced by sequential tephra blanketing) and also the current chemical status of the soil would provide useful boundary condition information.
3) sampling and analysis of the $\delta^{13}C$ ratios in modern aquatic organisms, land plants and surface sediment material would help in constraining the interpretation of the $\delta^{13}C$ record, especially for the Holocene period.
4) particle size analysis of the sediment zones around tephra layers and on the turbidite sequence in conjunction with thin section examination would improve our insight into the processes of sedimentation in the system and their link with climate.
5) a more detailed stable isotopic study of the calcite layers might yield interesting palaeohydrological information.
6) study of the diatom record would greatly compliment the pollen and geochemical records in terms of reconstructing the chemical and physical conditions of the lake waters. Samples

have already been 'rescued' for this at Durham and are awaiting financial support for a student or research assistant to carry out the work.

7) a recent study into the possible processes of diagenetic sulphur and nitrogen enrichment using stable isotope and radio-tracer techniques would document what may be a relatively pronounced diagenetic phenomena connected with this type of volcanic setting.

8) ultimately it would be nice to recover a core to the base of the maar sediment sequence in order to thoroughly appreciate the history of this depositional environment. Logistically this would be easier to accomplish using a civil engineering type drilling rig at the lake edge, although a high quality piston core taken below the central part of the lake would be more desirable given the resources. In addition, there is scope for more field investigation into the nature of the deep cauldron feature perhaps using sonar equipment and diving operations.

APPENDIX 1

PROCEDURES

SAMPLING

Sampling began on Core C which covers the upper part of the record, to be exact from 168cm to 1542cm depth. It was originally intended to sample every 5cm or 10cm using plastic cylinders to remove a plug of material at regular intervals. However, due to the high water content of the sediments in this part of the profile, it became clear that this would not provide sufficient dry material to carry out the planned analyses (most particularly X-ray fluorescence spectroscopy). Therefore the coarser 10cm resolution was adopted and moreover it was necessary to excavate entire quadrants from the half-cores available. Typically, 100g of wet sediment was being taken and, on drying, was providing 10g of solid to work with. There is a potential risk concerning contamination of the sample by using its 'outer skin'. For example, the coring tubes had been lightly lubricated with an oil. This effect was taken into consideration when carrying out organic geochemical work later on, but was not felt to be a significant cause of error for most of the measurements that were to be made. Thus 10cm continuous sampling provided an initial 141 data points.

The wet sediment removed was placed on a watch glass and weighed. It was then dried in an oven at 50°C for 48 hours. This relatively low temperature was used to minimise the loss of any labile/volatile organics etc.. When the sample had been dried it was weighed again, enabling the water content to be calculated.

The next step involved grinding the dry sediment brick for 75 seconds in a Tema® tungsten carbide mill. This provided a well-blended and homogeneous fine powder on which subsequent analyses were based. The grinding step should be carried out for as short a time as is possible since the process may cause possible damage to certain mineral structures (e.g. clays) and generates heat which could have an undesirable effect on the more sensitive chemical constituents in the sample (Fairchild et. al., 1988). It may be preferable to grind the sample by hand in an agate pestle and mortar, though the amount of time that would be required to handle the sample quantities in this study lead to a compromise.

The ground powders were stored in labelled plastic jars with the lids screwed down tightly. Samples were given names relating to their absolute depth from the top of the sediment sequence. The mid-point depth of each 10cm chunk was chosen for this categorisation.

Later in the project, when palaeomagnetic work had been completed on sample cubes from Core D, it became possible to extend the geochemical investigations to the whole 51m of profile. Material from these palaeomag sample cubes would provide fairly complete coverage of the interval from 16m depth down to the base at 51m. It was decided to continue working with an approximately 10cm sampling resolution. This strategy had brought out clear and often detailed trends from the results on the upper section, and represented a reasonable maximum quantity of samples that could be submitted for XRF work.

Firstly the new material (inside perspex cubes) was weighed and dried out under similar conditions to above. The sample lids were removed to facilitate the drying process. In order to provide a comparable spacing, batches of four or five adjacent sample cubes were combined, after drying, by grinding together in the Tema mill. Due to the size of these cubes (~2.25cm), this scheme provided adequate quantities of dry material at a 9 or 10cm resolution. Again, the resultant 286 jars of ground sample were labelled with a mid-point depth calculated by averaging the depths of the component sample cubes incorporated.

It was necessary to use material from Core E to complete the top 170cm of the profile. This was kindly provided by Bernd Zolitschka, who removed 17 samples from a half-core in Trier University. The samples consisted effectively of 10cm chunks/quadrants similar in nature to the samples removed from Core C initially. They were sealed in polythene bags and sent to Edinburgh whereupon they were weighed, dried and ground in similar fashion to above.

These preparations resulted in a data set containing 444 samples of bulk sediment at well-spaced intervals through the entire 51m profile, with only a few minor gaps present. The following analyses were made on either the entire data set or on a representative selection of points.

CHEMICAL ANALYSES

XRF

To begin with, it was decided to measure a range of major and trace element concentrations in the samples using X-ray fluorescence (XRF) spectroscopy. This is a highly automated technique which is ideal for the multi-elemental analysis of many geological materials.

Sample preparation involved the manufacture of pressed powder discs for trace element analysis and fused glass discs for the major elements. Small-diameter pressed powder discs were made using 3.3 to 3.4g of sample powder and boric acid as a surrounding case. It was not necessary to add a binding agent as clay and other constituents in the sample adequately held the disc together. While awaiting measurement, the discs were stored in a desiccator to prevent clay swelling and damage. The pressed powder discs were run through the BRIMO and RHSMALL analysis programmes (see Table A.1.) on a Philips PW 1480 spectrometer. This allowed the measurement of 21 trace elements and also gave a crude estimate of the 10 major elements' concentrations. The BRIMO run was executed first because it involved the determination of iodine which is particularly volatile and may undergo progressive loss as X-ray bombardment heats up the sample surface.

BRIMO

I	±7ppm
Br	±2ppm
Mo	±1ppm
Zr	±4ppm

RHSMALL

Sc	±4ppm	Zn	±2.2ppm
Ba	±27ppm	Pb	±2.4ppm
V	±7ppm	Th	±2.1ppm
La	±8.5ppm	Rb	±2ppm
Nd	±5.5ppm	U	±2.3ppm
Ce	±14ppm	Sr	±3.3ppm
Cr	±2.2ppm	Y	±1.1ppm
Ni	±2ppm	Zr	±3.5ppm
Cu	±1.1ppm	Nb	±1.2ppm

SCL

S	±0.08wt%
Cl	±31ppm

Table A.1. Precision data (as 2σ std deviations) for XRF analysis programmes

At a later stage, the pressed powder discs were run through a third analysis programme (SCL) to measure sulphur and chlorine. For sulphur, count rates were normalised to the Rh L_α tube line to make a rough compensation for mass absorption phenomena (WIlliams, 1987). It is thought that wavelength shifts of the S K_α doublet (due to variable oxidation states of sulphur) could cause error in quantitative analysis (Elsheimer and Fabbi, 1974). This may be due to overlap of spectral lines leading to increases in emission line intensity. These effects were not considered significant for the comparative data being sought in this study. Gohshi et. al. (1975) succeeded in resolving sulphate sulphur from sulphide sulphur in samples using a high resolution spectrometer. However, in this study the collimator used is relatively coarse and a single peak (representative of total sulphur) was measured.

For chlorine the calibration line was composed of a number of low-Cl rock standards, but contained only one standard with high Cl content. Effectively, a two point calibration was being used to compare sample counts against. Thus the possibility of the line being poorly defined (and ∴ providing less accurate measurements) was higher.

Machine precision is easily checked by running selected discs six times in succession. The 2σ standard deviations in ppm are presented in Table A.1. Machine precision is generally very high, with the exception of iodine and chlorine. Chlorine suffers from the same atomic effects associated other light elements such as Na and Mg (Williams, 1987). Since it is only present in trace amounts, these effects have a more serious influence on its measurement problems. Iodine is present in very low concentrations (<10ppm). Although it is a heavy element, its measurable peak is situated in an area of high background counts. Therefore the error associated with subtracting one large number from another is high in comparison with the value being determined.

In order to estimate the manufacturing precision it would have been necessary to produce five or more discs from the same sample powder for measurement. However, with the limited material available it was only possible to prepare single discs and so this was not calculated. It is thought that errors arising from sample preparation would be similar to or possibly larger than machine errors, though not large enough to significantly affect data interpretation. As the data obtained in this study are being used to examine trends and changes rather than to model and quantify processes, accuracy was not evaluated. Accuracy is generally considered to be better than ±5% relative to the measured value (D. James, pers. comm.). Later investigations of sulphur, chlorine and silica by wet chemistry provided results that corresponded satisfactorily with the XRF concentration data.

Manufacture of fused glass discs involved a 'pre-ignition' stage. This is advisable when sample materials contain appreciable concentrations of organic carbon which could destroy the platinum crucibles that are used. A few grammes of sample powder was thoroughly dried in an oven at 110°C for 4 hours before being placed in a silica crucible and weighed. The crucible was placed in a furnace at 1100°C for 25 minutes. During this time volatile components (organic matter, inorganic nitrogen, bound H_2O, iodine, sulphur, etc.) were lost from the sample. The resultant ash was cooled in a desiccator and reweighed allowing the loss on ignition (LOI) to be calculated. Between 0.9 and 1.0g of the ash was placed in a platinum crucible and diluted with a 5:1 ratio of Spectroflux 105® (a mixture of lithium tetraborate, lithium carbonate and lanthanum oxide). Flux and sample were well mixed with a platinum stirring rod before being fused in a furnace at 1100°C for 20 minutes. It was necessary to add a further small amount of flux after this stage because the original body of flux loses water vapour that it has earlier absorbed while in the furnace. With the now accurately diluted sample the crucible was reheated on a Bunsen and swirled to ensure complete mixing. The molten glass was then cast into a disc which required annealing for 15 minutes on a 220°C hotplate. In general, the discs formed cleanly on their first casting. Occasionally it was necessary to recast a disc that had shattered while cooling.

The glass discs (stored in a desiccator while awaiting measurement) were analysed by the MAJORS programme (see Table A.2.). The machine precisions shown in the table (2σ standard deviations in wt%) are very high. It is thought that manufacturing processes in the fusion stage would represent a greater source of error, but not significant enough to affect the data interpretation.

MAJORS			
SiO2	±0.1wt%	Na2O	<±0.01wt%
Al2O3	±0.02wt%	K2O	<±0.01wt%
Fe2O3	±0.01wt%	TiO2	<±0.01wt%
MgO	<±0.01wt%	MnO	<±0.01wt%
CaO	±0.01wt%	P2O5	<±0.01wt%

Table. A.2. XRF precision data (as 2σ std deviations) for major elements

Total C & N and Total S

Total carbon and total nitrogen were determined on a Carlo Erba® NA-1500 elemental analyser. The arrangement used involved an oxidation column packed with chromium trioxide and silvered colbaltous cobaltic oxide, a reduction column packed with copper wire and a furnace temperature of 1050°C (see Verardo et. al., 1990). The GC column oven was set at 45°C. Between 5 and 25mg (but less than 10mg if more organic-rich) of sample powder was weighed into a tin foil capsule and presented to the machine. Results regularly have a precision (percent relative standard deviation, 1σ) of ±1.5% for carbon and ±4% for nitrogen.

Precision was marginally higher for samples with higher concentrations (>5wt% C) of organic matter. Acetanilide and Sulfanilamide synthetic standards were used to calibrate the machine.

The measurement of total sulphur was later attempted on the same machine. Total sulphur had not previously been attempted on the Carlo Erba at Edinburgh, though other Carlo Erba users have successfully carried out the analysis (e.g. Leeder et. al., 1990). Firstly the oxidation and reduction columns were replaced with a single tube packed with tungstic anhydride, tungstic anhydride on alumina and copper wire. This was connected to the chromatographic separation column. The chromatographic column oven was this time set at 85°C while the furnace remained at 1050°C. Between 5 and 25mg of sample powder was weighed into a tin-foil capsule and presented to the machine.

After some intitial adjustment to the experimental conditions, the analysis appeared to be running well. To begin with chromatograms with well-defined sulphur peaks and stable, low baselines were observed. However, after the first few sample runs the results began to look unreliable. Also standards such as Mag-1 were giving values far too high. Double peaks were appearing and baselines drifting strongly. It was thought that the combustion reaction was not occurring properly and that perhaps the sulphur dioxide was being liberated gradually, or that somehow sulphur trioxide was being allowed to enter the column. Vanadium pentoxide, which is a routine accelerator for total sulphur analysis (e.g. Hall and Vaive, 1989), was added to the samples before combustion, though this did not lead to an improvement. After several more unsuccessful attempts to return to a clear signal the analysis was abandoned.

Later, when sulphur had been analysed by XRF, it was found that a reasonable match existed between the XRF results and the early results obtained by the Carlo Erba, apart from differences in absolute values. This gave confidence that both techniques were identifying the correct trends in the sediment profile.

Inorganic carbon

A simple pressometric technique similar to that described by Jones and Kaiteris (1983) or Presley (1975) was employed to measure inorganic (carbonate) carbon content. Between 100 and 330mg of sample powder was reacted with 50% phosphoric acid and the amount of carbon dioxide evolved measured by manometer. The manometer scale was calibrated using ANALR® anhydrous $CaCO_3$ as a standard. All sample-acid mixtures were brought to boiling point several times with a small Bunsen to ensure complete reaction of the carbonate minerals present. It was noted that samples from 13m to 23m depth typically showed a strong reaction as soon as the cold acid was tipped over. On the other hand, many of the samples below 23m depth showed no reaction with cold acid, but reacted vigorously when warmed. These observations suggest the respective dominance of calcite and siderite as the main carbonate phases in the sample (Hillebrand, 1953). Most samples covering the top 12m were thought to contain little or no inorganic carbon and were dealt with more rapidly. Generally no reaction was observed and the manometer was not deflected beyond the normal blank displacement. Therefore these samples contain quantities below the detection limit of 0.06wt% C, or are carbonate-free. Selected samples were run five times in order to assess precision. This was calculated to be ±1.7% or better, relative to the measured value. Such values compare favourably with the precisions for total carbon measurements obtained on the Carlo Erba. A kimberlite standard run as an unknown indicated that accuracy was around ±1.5% relative to the real value.

The acid reaction is capable of liberating H_2S gas from any monosulphides of iron present in the sample (Hillebrand, 1953). This could cause carbon dioxide values to be overestimated through extra deflection to the manometer reading. None of the samples when treated with acid displayed an obvious smell suggesting the presence of significant hydrogen sulphide. However, some samples in the upper part of the core gave a weak suggestion of the gas being present and so may have liberated a minor amount of H_2S. It is believed that effects of this on the carbon dioxide measurements would be minimal and in the sub-detection level range.

Organic carbon

By subtracting the values for inorganic carbon content from total carbon a measure of the organic carbon content was found.

Biogenic silica

Biogenic silica was analysed by wet chemistry using an alkaline leaching technique and colourimetric determination of the resulting silica solution. The method was based on that described by Eggimann et. al. (1980), being adapted at Edinburgh by Mike Saunders.

Between 45 and 60mg of sample powder was weighed into a 40ml PTFE digestion cup and 20ml of saturated (2M) sodium carbonate solution added. The cup was sealed inside a stainless steel bomb and placed in a 100°C oven for 4 hours. These conditions ensured a thorough reaction digesting all of the amorphous silica present in the sample, but with minimum digestion of quartz or silicate minerals present. The resulting solution was passed through a 0.45μ filter and the filtrate plus washings collected and made up to 100ml with distilled water.

Solutions were analysed for silica content and later for alumina content (to provide a correction for small amounts of aluminosilicate that may have been leached from the sample). Silica was determined by formation of the molybdenum blue complex (method modified from Strickland and Parsons, 1968) and measured in 2cm spectrophotometer cells at a wavelength of 812nm. Aluminium was determined through formation of the catechol violet complex (method modified from Dougan and Wilson, 1974) and measured at 585nm in 1cm cells.

Apparent biogenic silica (i.e. the silica value measured) was converted to actual biogenic silica using the following correction:

$$\text{actual biogenic silica (wt\%)} = \text{silica measured (wt\%)} - \mathbf{n} * \text{alumina (wt\%)}$$

$$(\mathbf{n}=2.8)$$

The value for **n** is chosen to reflect the likely silica/alumina ratio of the mineral fraction in the sediments. This generally lies between 2 and 3. The value of 2.8 was selected after examining the XRF data for variations in the range of total silica/alumina ratios. It is likely that such a ratio will never be identical for any two samples, but as this calculation only makes a small correction to the apparent silica value, such variations will not affect the final results significantly.

After completing an initial batch of measurements on the top 99 samples in the profile, a later batch of samples was taken from 60 selected positions covering the rest of the profile. A number of the samples were repeated five times to assess precision. This was calculated to be ±2% or better, relative to the measured value. Some of the discrepancy in values could be attributed to sample inhomogeneity (Mortlock and Fröelich, 1989). This is due to the small sample quantity being taken for the measurement.

It had been found that the initial results matched very well with values predicted by normalising the XRF data for "excess silica." (see Chap4a). The later set of 60 samples did not correspond quite as well to their XRF predicted values, but a good overall correlation still existed. From this it was decided that the XRF data could be used to provide a reliable guide to trends in the biogenic silica content of the core sequence.

Stable carbon isotopic ratio of bulk organic matter

Around 30 samples were initially selected for isotopic analysis of the organic carbon present. A quantity of sample powder (2-3g) was washed with an excess of 1M HCl to remove **all** inorganic carbon present. This involved adding the dilute acid with a pipette until no further effervescence occurs. To encourage a complete reaction, the sample was placed in a vacuum oven at room temperatue for 25 minutes and later evaporated to dryness in a conventional oven at 50°C. Up to 100mg of dry and treated sample was placed in a silica tube together with an excess of copper oxide. The tube was evacuated and roasted overnight at 850°C to oxidise the organic matter. The carbon dioxide produced was purified on a vacuum line apparatus by means of cryogenic distillation. The purified gas was collected in another tube and transferred to a VG Isogas SIRA10® mass spectrometer for isotopic determination. The $\delta^{13}C$ ratios measured are equated relative to the PDB standard. This work was carried out at SURRC in East Kilbride.

Later in the study, further sample batches were analysed to produce a more detailed isotopic profile. For some of this work a slightly different technique was applied to remove inorganic carbon. It had become clear that siderite was present in some parts of the core and that this requires warming of the acid-sample mixture to near boiling point to ensure complete removal (Hillebrand, 1953). Therefore later samples were treated with dilute hydrochloric or phosphoric acid and warmed on an electrically heated sandbath at approximately 80°C. For comparison, some of the earlier samples were redone under these more intense reaction conditions. It was found that most of these gave the same isotopic value, although a few samples produced a lighter $\delta^{13}C$ value which might be expected if some 'heavy' carbonate carbon had previously remained.

Over four visits to SURRC it was possible to construct a $\delta^{13}C$ record containing 110 data points. Throughout the study triplicate samples were run to check precision. This worked out at being ±0.2‰ or better. Accuracy was assessed by running an in-house graphite standard between samples and was evaluated at being ±0.2‰.

Carbonate stable isotopic studies

A short study was made of the stable isotopic compostion ($\delta^{13}C$ and $\delta^{18}O$) of some carbonate minerals in the profile. Both calcite and siderite were known to occur from X-ray diffraction. Although either calcite or siderite is dominant in most of the carbonate areas, it is desirable to apply some segregation technique to allow isotopic values to be determined on pure individual phases. To begin with, mineral separation using a heavy liquid and centrifugation was applied. Tetrabromoethane ('TBE', sp. gr. 2.96) was judged to be an appropriate liquid to use since the densities of calcite and siderite are 2.7 and 3.7-3.9gcm^{-3} respectively. Several grammes of a sample with high carbonate content was tested using a Hutton tube arrangement (Allman and Lawrence, 1972). After centrifugation at 2600rpm, a small quantity of 'heavy fraction' was observed in the bottom chamber of the Hutton tube. This was recovered and examined by XRD. Results showed that the dominant minerals present were siderite (as anticipated) and augite. However the heavy fraction appeared excessively small and, when the larger 'light fraction' was examined with XRD, it was found to still contain a large proportion of the siderite. The light fraction was reprocessed using more prolonged centrifugation, but this separated out virtually no further siderite. Therefore it was possible to isolate a pure quantity of the siderite fraction (N.B. this might not be isotopically representative of the whole), but it had not been possible to separate pure calcite into the light fraction. It is thought that the very fine grain size of the sample material and perhaps also the cohesive properties of components within, such as organic matter and clays, might be holding some of the siderite among the light fraction. This material may be very difficult to disaggregate and thus to wet all grains with the separating liquid. In theory, using long centrifuge runs at much higher rotating speeds (Allman and Lawrence, 1972) might permit a quantitative separation to be made, though this was not possible with the equipment available.

As an alternative, bulk samples were run through a sequential reaction programme with 100% phosphoric acid, based on Rosenbaum and Sheppard (1986). Firstly, samples were reacted with 'cold' acid at 25°C for 3 hours. Reactions involved 50 to 200mg of sample powder in an evacuated glass tube. This allows quantitative conversion of calcite to CO_2, but has a minimum effect on siderite present. The carbon dioxide formed at this stage was released into a vacuum-line apparatus for purification. A similar cryogenic distillation technique to that used for the organic $\delta^{13}C$ study was applied. The purified gas was collected in a sample tube and transferred to a VG Isogas SIRA10® mass spectrometer. The $\delta^{13}C$ and $\delta^{18}O$ values measured are relative to the PDB standard.

After collection of the gases, the re-evacuated tube was sealed and placed in a water bath at 98°C. Acid and sample were allowed to react at this temperature for 45 hours. Under these conditions the siderite present was quantitatively converted to CO_2. This new yield of carbon dioxide was purified and measured on the mass spectrometer as previously.

For comparison, a few samples were run through a single 17 hour reaction with the water bath at 140°C. This causes all carbonate phases to react, the resultant carbon dioxide having multiple origins. Also, two extracts of siderite produced by the heavy liquid separation contained sufficient carbonate material for an analysis and so were run through this reaction. Isotopic ratios were determined as before.

During the sample reactions an in-house calcite standard was run to check accuracy. This was calculated to be ±0.2‰ or better. Samples run in triplicate gave an estimate of precision of ±0.2‰ or better.

Chlorine

A small number of samples were analysed for chlorine by a wet-chemical technique This is a relatively accurate analysis and should thus assess the accuracy of the XRF results. The technique involved an alkaline fusion (Jeffery, 1970), using a flux mixture of Aristar sodium carbonate and zinc oxide, followed by spectrophotometric determination using the mercury(II)thiocyanate method (Florence and Farrar, 1971). The U.S. granodiorite standard GSP-1 (400ppm Cl) was also run as a check. Results obtained are shown in Table A.3. below:

Sample	Cl ppm	Cl ppm (XRF)
65	270	275.0
1746	140/160	95.2
4496	230	177.0
1453	3600	4524.8
2470	3500	4076.9
VUL2	4500/4500	5892.2
GSP-1	390	---

Table A.3. Wet chemical determinations of chlorine content

The concentration figures for the six samples are similar in magnitude to the corresponding XRF results, although Cl-rich samples show a tendency to be over-estimated by the XRF method. This may be due to calibration problems previously explained. At the lower concentration end, discrepancies may arise due to the limits in sensitivity of the XRF measurement. However, although the discrepancies are often appreciable, they are unlikely to affect the basic trends that chlorine is displaying in the core profile.

Iodine

Due to the low iodine content of these freshwater sediments, and the difficulty in obtaining accuracy with the XRF measurement, it was decided to investigate a small number of the samples with a more sensitive wet chemical technique. This involved alkali fusion of the bulk sample followed by colourimetric determination of the iodine content by absorbance (Grimaldi and Schnepfe, 1971). A flux of sodium carbonate, potassium carbonate and magnesium oxide (in the ratio 4:4:1) was made up and mixed together thoroughly. Approximately 1g of sample powder and 4.5g of the flux were blended together in a nickel crucible. This was fused at 750°C in a furnace for one and a half hours. The sinter produced was covered with water and left overnight, allowing complete disintegration. The leached solution was filtered and made up to fixed volume (100ml). The iodine in this solution was converted to the elemental form and taken up in 3ml of carbon tetrachloride following Grimaldi and Schnepfe (1971). The absorbance of the resulting solution was measured by spectrophotometer in 4cm cells at 517nm. A series of potassium iodide standard solutions were prepared for calibration purposes.

Unfortunately the results obtained were spurious, probably due to the ideal photometric cell type being unavailable. However, comparison of the values recorded and also visual comparison of the colour intensity of solutions before measurement suggested that the sample solutions contained somewhat lower iodine contents than the weakest standard. Consequently, these samples are believed to contain less than 10ppm iodine. In future it might be possible to measure this type of sample more accurately with a newly produced set of photometric cells that are available (M. Saunders, pers. comm.).

Pyrolysis

Around 150 samples were analysed by pyrolysis on a LECO® THA-200 "Thermolytic hydrocarbon analyzer". This is a routine technique developed to assess the concentrations of free and bound hydrocarbons in whole-rock samples (Espitalié et. al., 1977). Typically, 100mg of sample powder was loaded into a crucible and presented to the machine, but for organic-rich material 30-40mg was used. During a progressive heating programme, free hydrocarbons (the S1 peak) are released between temperatures of 100 and 300°C. Between 300 and 550°C further hydrocarbons (the S2 peak) are released through cracking of the kerogen component. The quantities of hydrocarbon released are determined by a flame ionisation detector. A standard oil shale, KC8, was used to calibrate the machine. Samples replicated five times showed that precision was around ±5% relative to the measured value.

By normalising the content of kerogen-derived hydrocarbons to total organic carbon, the hydrogen index (HI) of the samples was calculated. This parameter is strongly related to the elemental H/C ratio of the kerogen (Miles, 1989) although the latter would be much more time consuming to measure.

Organic geochemical molecular investigations

Ground, dried sediment was again required for the initial lipid extraction stage of this work. For sample points produced from the palaeomag cubes of Core D, direct use was made of the dried ground powder from the sample jars. However, for samples in the upper 15m of the profile which had been produced from entire quadrants in the sediment core, it was thought that the inclusion of the outer skin in the sample might seriously contaminate the small quantities of lipids being analysed. Therefore, new samples were made up for these points by taking new wet sediment (available from spare palaeomag cubes covering this depth range). Cubes from both Core C and Core D were used. After the sediment in the cubes had been dried out at 50°C it was ground (on this occasion by an agate pestle and mortar) into a powder ready for the following extraction.

Between 5 and 30g of sediment powder was weighed into a cellulose (compressed paper) thimble, plugged with cotton wool and suspended in a glass beaker. The beaker was filled up with a solvent mixture (93:7) of dichloromethane (DCM) and methanol and placed into a Soxtherm® apparatus. The contents of the beaker was heated from below by an oil bath and allowed to boil/reflux at 45°C for 4 hours. During this time, extractable components within the sediment organic matter (i.e. free lipids) were liberated. The solvent+extract was subsequently reduced down to a small volume and quantitatively transferred to a glass vial. Throughout these procedures, all of the glassware used had been previously cleaned in chromic acid and washed with pure DCM to avoid contamination. The cellulose thimbles and cotton wool were also refluxed thoroughly with pure solvent beforehand. The solvents used had been purified by double distillation.

The total extract obtained by the above process was next separated into three fractions by column chromatography on activated silica gel and alumina. The aliphatic hydrocarbon fraction discussed in Chap. 5 was eluted with 120ml of petroleum ether. (Further fractions were eluted in sequence with petroleum ether/DCM (50:50) and DCM/methanol (50:50) to recover respectively the aromatic hydrocarbon and polar groups.) Gas chromatographic analysis of the aliphatic fraction was carried out on a HP 5890 GC fitted with a 30m J&B DB5 fused silica capillary column. On-column injection was used and hydrogen acted as a carrier determined by flame ionisation detection (FID). Most of the GC analytical work on these samples was carried out by Bernie Bowler at the organic geochemistry department (NRG) of Newcastle University. The author gratefully acknowledges this work.

Investigation of samples of volcanic rock from the catchment

A suite of ten rock samples was collected with the help of Giuseppe Dai Pra during the coring fieldwork. These originate from roadside exposures within the Monticchio crater or from the surrounding Vulture mountains a few kilometres away. Thin sections of the rocks were prepared by Simon Harley and Jane Foster. The sections were examined with a petrographic microscope.

It was considered that these lithologies should reflect the typical catchment rock which, through processes of weathering etc., will eventually enter the lake sediment system as the terrigenous minerogenic fraction. Thus, it was decided to investigate the chemical composition of this material for comparison with the compositions found in the lake sediments. After examining the ten thin sections, two samples (known as VUL2 and VUL4) were selected due to their relatively unaltered appearance. The outer skins of the samples were trimmed off and the samples crushed manually before being ground for four minutes in a Tema mill. The ground sample powders were subjected to XRF, Total C and N, and inorganic carbon determinations in the same way as the sediments.

XRD Mineralogy

Samples were examined on a Philips PW 1800 X-ray diffractometer to assess their minerological compositions. In most cases, ≈1g of sample powder was compressed into a powder disc and presented to the machine embedded in a sample holder. Occasionally, smaller quantities of sample were extracted from fresh core material, taken up as a suspension in acetone or distilled water and coated on a glass disc. On drying, the disc was placed in a larger sample holder and presented to the machine. An on-line mineral reference library was used to qualify the likely minerals present from the raw diffraction trace data.

Optical examination of diagenetic minerals

Thin sections prepared for varve analysis were examined with advice from Bernd Zolitschka while on a visit to Trier University. Notes and observations made during this visit form part of the discussion in Chap 4c.

Palynofacies organic matter studies

Microscope slides were prepared from various regions of the core in order to examine the nature and quality of the organic matter present. The preparation techniques are similar to those used in palynolgical investigations (e.g. Traverse, 1988).

Approximately 5g of unground, wet sediment was placed in a large plastic beaker and dispersed into small fragments. An excess of hydrochloric acid was added to remove carbonates. After rinsing the sample with distilled water, 40% hydrofluoric acid was added and the beaker allowed to stand for 48 hours. During this time most of the inorganic mineral components and the biogenic silica were digested. After several more rinses a further quantity of hydrochloric acid was added to remove any fluoride minerals that may have formed. The residue, consisting mostly of organic matter, was washed through in a 10µ mesh sieve. This removed very fine, undefined organic material which cannot be identified. The organic concentrate was stored as a slurry in distilled water.

To make up a slide, 15ml of slurry was pipetted into a small quantity of hot glycerol (at 65°C) and mixed together. A fraction of this was coated onto a glass cover slip and, after drying, stuck down onto a microscope slide. The slides were examined with a petrographic microscope under normal transmitted light and u.v. stimulated fluorescence illumination. Identifications were made with assistance from Richard Tyson and from consulting standard texts (Combaz, 1981; Berglund, 1986; Faegri and Iversen, 1965; Bold and Wynne, 1985; Gray, 1960). Preliminary point counts were made on a rectangular stage.

Electron microscopy

Representative samples of unground core material were selected for examination by scanning electron microscopy. Small sections of wet sediment were removed and dried overnight in an oven at 50°C. The dried 'brick' was carefully broken open to reveal a fresh surface and mounted on an aluminium stubb using araldite. The base region of the sample and stubb were coated with a silver paint to reduce charge build-up while inside the microscope. The entire sample surface was also gold coated for similar reasons. The samples were then examined by a Cambridge Instruments® S90b scanning electron microscope in the Department of Botany at Edinburgh University. Photographic images were made of specimens by means of an attached camera.

Radiocarbon dating of plant macrofossil and bulk samples

While the cores were being extruded and subsampled during Sept 1990, a number of layers containing plant macrofossil material were observed. These were between 0.3 and 4cm in thickness and either consisted of bryophytic mats or more heterogeneous terrestrial plant matter that was often associated with tephra horizons. Material from such layers was removed and placed in sealed polythene bags for possible radiocarbon dating. After the sample bags had been returned to Edinburgh they were kept in a dry refrigerated store at 4°C.

During October 1992 selected samples were examined by Brian Huntley and Judy Allen at Durham University. Appropriate material was extracted (mosses of terrestrial/fen origin and definite terrestrial plant remains) and submitted for a.m.s. radiocarbon dating. The dating was carried out at Tuscon (USA) after pre-treatment work at the NERC laboratory in East Kilbride. The samples dated are shown with error margins in Table A.4. below. Also included at the bottom of this table are a series of three conventional bulk dates made on the sequence by W Watts.

Sample	Depth	Age (yr)	Error (+/-)
LGM7	945cm	32,630	630
LGM10	1073cm	29,900	410
LGM21	1403cm	33,350	620
LGM12	1618cm	31,830	550
LGM16	1853cm	34,775	725
LGM18	2351cm	25,200	250
MONT1	724-740cm	30,460	510
MONT2	653-663cm	23,670	230
β61220	398-403cm	7,130	120
β61221	820-825cm	15,380	150
β61225	1316-1320cm	19,580	730

Table A.4. Radiocarbon dates for Monticchio samples and associated error margins

APPENDIX 2

TABULATED DATA

Tabulated data

The following pages present chemical data in a tabulated form. The concentration values shown are related to sample depths in the far left hand column. The measurement techniques and error bars have been described in Appendix 1. The following abbreviations and concentration units apply:

depth	cm		
Si	wt%	Pb	ppm
Al	wt%	Th	ppm
Fe	wt%	U	ppm
Mg	wt%	Rb	ppm
Ca	wt%	Sr	ppm
Na	wt%	Y	ppm
K	wt%	Zr	ppm
Ti	wt%	Nb	ppm
Mn	wt%	Cl	ppm
P	wt%	S (by XRF)	wt%
Sc	ppm	Ctot (total carbon)	wt%
Ba	ppm	Ntot (total nitrogen)	wt%
V	ppm	Sulp (Carlo-Erba S)	wt%
La	ppm	Cinorg (inorganic C)	wt%
Ce	ppm	LOI (loss on ignition)	wt%
Nd	ppm	water (content)	wt%
Cr	ppm	I	ppm
Ni	ppm	Br	ppm
Cu	ppm	Mo	ppm
Zn	ppm		

del C-13	δ^{13}C value on bulk organic matter (‰ relative to PDB standard)
Bsilica	biogenic silica (wt%)
HI	Hydrogen Index (mg hydrocarbon/g total organic carbon)

depth	Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn	P
5.0	22.76	5.86	4.22	2.25	5.98	1.05	3.275	0.361	0.110	0.236
15.0	19.93	1.38	2.83	0.30	2.11	0.20	0.473	0.080	0.242	0.150
25.0	16.72	1.34	2.59	0.30	6.59	0.15	0.384	0.073	0.161	0.121
35.0	19.27	1.43	2.71	0.28	6.02	0.14	0.368	0.078	0.166	0.150
45.0	22.76	1.14	3.31	0.19	2.09	0.11	0.306	0.063	0.127	0.219
55.0	28.99	0.92	1.93	0.18	0.79	0.11	0.344	0.055	0.040	0.081
65.0	30.58	0.86	2.13	0.20	0.71	0.14	0.346	0.055	0.053	0.086
75.0	26.25	1.40	2.75	0.30	0.70	0.17	0.587	0.091	0.068	0.101
85.0	24.76	1.13	2.59	0.24	0.57	0.12	0.414	0.061	0.091	0.102
95.0	25.77	0.69	2.68	0.29	1.12	0.14	0.236	0.035	0.287	0.187
105.0	27.21	4.38	2.94	1.03	2.85	0.82	2.604	0.226	0.093	0.164
115.0	23.60	8.14	4.15	2.15	5.70	1.70	5.176	0.400	0.109	0.281
125.0	26.33	1.72	2.34	0.58	1.62	0.31	0.822	0.097	0.059	0.111
135.0	29.92	0.74	1.79	0.17	0.58	0.12	0.206	0.041	0.057	0.074
145.0	30.41	0.71	1.48	0.17	0.53	0.12	0.204	0.041	0.055	0.069
155.0	28.64	0.78	1.57	0.17	0.48	0.11	0.225	0.046	0.042	0.074
165.0	29.20	0.90	1.58	0.19	0.49	0.11	0.295	0.052	0.036	0.075
183.0	27.54	0.88	1.77	0.20	0.55	0.10	0.264	0.050	0.031	0.068
193.0	26.56	0.95	1.59	0.21	0.55	0.11	0.257	0.056	0.035	0.066
203.0	29.20	0.80	1.62	0.16	0.49	0.11	0.213	0.050	0.029	0.062
213.0	30.29	0.67	1.50	0.19	0.42	0.10	0.202	0.039	0.024	0.054
223.0	25.25	1.33	2.30	0.24	0.59	0.14	0.397	0.072	0.041	0.072
233.0	25.47	1.77	2.56	0.28	0.64	0.18	0.518	0.094	0.077	0.085
243.0	26.04	2.43	2.42	0.26	0.63	0.63	1.019	0.112	0.052	0.075
253.0	25.04	1.24	2.37	0.24	0.58	0.12	0.374	0.068	0.042	0.077
263.0	25.97	1.12	2.10	0.21	0.51	0.11	0.333	0.063	0.035	0.068
273.0	22.34	0.92	2.44	0.22	0.55	0.07	0.254	0.053	0.034	0.072
283.0	22.87	0.88	1.96	0.19	0.48	0.09	0.243	0.052	0.028	0.053
293.0	25.69	0.84	1.27	0.19	0.43	0.08	0.253	0.049	0.023	0.050
303.0	27.67	1.33	1.65	0.22	0.54	0.14	0.493	0.069	0.027	0.062
310.5	24.43	5.08	3.41	0.68	1.97	0.90	2.689	0.213	0.051	0.213
315.5	24.16	9.82	3.47	1.30	3.89	2.14	5.743	0.396	0.085	0.260
320.5	24.51	9.76	3.65	1.53	3.84	2.30	5.606	0.379	0.087	0.222
327.5	27.09	2.49	1.44	0.39	0.89	0.45	1.176	0.100	0.031	0.118
335.5	24.50	9.60	3.34	1.84	4.09	2.06	5.520	0.373	0.078	0.249
343.0	22.85	1.36	1.73	0.26	0.68	0.16	0.438	0.064	0.028	0.080
353.0	23.26	3.26	2.12	0.50	1.27	0.75	1.576	0.105	0.041	0.145
362.5	18.36	1.76	2.45	0.24	0.70	0.24	0.655	0.077	0.033	0.085
377.0	21.33	5.09	2.59	0.65	1.71	1.12	2.972	0.189	0.054	0.143
387.0	16.80	1.74	1.70	0.25	0.76	0.28	0.670	0.078	0.034	0.084
397.0	20.75	1.00	2.23	0.21	0.67	0.16	0.346	0.049	0.030	0.075
407.0	22.96	1.39	3.92	0.26	0.92	0.16	0.408	0.077	0.041	0.107
417.0	14.36	0.99	3.47	0.19	0.65	0.10	0.261	0.052	0.029	0.085
427.0	16.30	2.27	2.36	0.30	0.95	0.38	1.101	0.103	0.035	0.087
437.0	23.05	0.82	1.20	0.15	0.49	0.12	0.278	0.040	0.020	0.060
447.0	24.82	3.73	1.74	0.31	0.99	0.91	2.286	0.135	0.041	0.078
457.0	15.01	0.76	2.95	0.26	0.71	0.08	0.182	0.039	0.028	0.074
467.0	18.86	0.60	1.85	0.19	0.64	0.08	0.155	0.034	0.024	0.068
477.0	14.06	1.23	4.18	0.21	0.74	0.26	0.615	0.055	0.030	0.072
487.0	17.41	0.49	2.68	0.15	0.54	0.09	0.164	0.026	0.041	0.069
497.0	15.64	0.59	2.98	0.15	0.59	0.13	0.209	0.030	0.051	0.083
507.0	17.68	3.84	2.60	0.28	0.83	1.48	1.955	0.152	0.082	0.084
517.0	15.72	0.32	4.27	0.15	0.63	0.07	0.107	0.019	0.060	0.523
527.0	24.16	0.25	2.80	0.12	0.42	0.06	0.079	0.016	0.055	0.089
537.0	29.43	0.17	3.40	0.11	0.32	0.04	0.065	0.016	0.123	0.534
547.0	23.70	0.20	5.23	0.11	0.34	0.04	0.073	0.017	0.202	1.152
555.0	22.24	0.24	4.87	0.11	0.39	0.05	0.085	0.019	0.252	0.999
562.0	17.33	0.24	7.52	0.13	0.45	0.05	0.076	0.015	0.216	1.681
577.0	15.81	0.82	10.19	0.19	0.64	0.18	0.397	0.034	0.259	2.498
587.0	16.73	0.50	6.39	0.16	0.57	0.14	0.212	0.020	0.306	1.175
597.0	18.54	0.65	4.93	0.17	0.60	0.15	0.272	0.026	0.463	0.507
607.0	16.80	0.88	8.57	0.18	0.65	0.19	0.344	0.027	0.563	1.636
617.0	16.78	1.44	10.56	0.20	0.79	0.28	0.653	0.042	0.445	2.502
626.0	21.38	6.82	4.31	0.82	3.20	1.66	4.069	0.203	0.216	1.070
634.0	20.47	2.73	5.01	0.28	1.12	0.72	1.207	0.069	0.392	1.144
642.0	20.86	5.81	4.04	0.69	2.53	1.83	2.987	0.149	0.230	0.912
649.5	24.82	9.70	2.70	0.72	2.63	3.95	5.005	0.205	0.109	0.267
657.5	22.86	7.10	4.59	0.74	2.26	2.70	3.520	0.184	0.162	0.793
667.0	20.45	2.61	5.89	0.24	0.79	0.66	1.498	0.084	0.233	1.128
677.0	21.50	4.92	6.16	0.34	1.03	1.27	3.217	0.153	0.136	1.284
687.0	15.78	0.37	3.21	0.15	0.55	0.08	0.121	0.020	0.120	0.130
697.0	16.38	0.35	4.92	0.16	0.52	0.11	0.120	0.022	0.168	0.523
707.0	19.18	0.46	5.32	0.15	0.49	0.07	0.116	0.027	0.169	0.425
717.0	21.95	0.52	5.32	0.15	0.47	0.07	0.149	0.031	0.133	0.136
727.0	24.03	0.64	4.26	0.15	0.43	0.07	0.177	0.035	0.066	0.088
737.0	26.92	0.86	2.69	0.16	0.43	0.11	0.301	0.047	0.045	0.085
747.0	27.91	3.36	2.37	0.34	0.91	0.62	1.549	0.152	0.044	0.396
756.5	27.91	4.16	2.89	0.40	0.98	0.51	1.561	0.222	0.046	0.369
776.5	27.50	5.80	2.55	0.63	1.47	0.98	2.807	0.256	0.042	0.322
785.0	25.93	8.80	3.14	0.87	2.50	1.83	5.628	0.313	0.075	0.274
794.0	27.80	3.42	2.53	0.40	0.76	0.41	1.243	0.174	0.048	0.155
804.0	25.29	3.50	3.19	0.46	0.71	0.29	1.001	0.189	0.083	0.231
814.5	22.03	3.74	4.52	0.49	0.91	0.40	1.316	0.174	0.225	0.419
825.0	17.65	1.91	7.22	0.37	0.74	0.18	0.529	0.103	0.281	0.274
835.0	20.59	1.80	6.68	0.33	0.63	0.17	0.482	0.100	0.157	0.211
845.0	27.85	2.60	1.67	0.28	0.50	0.53	0.895	0.133	0.067	0.133
855.0	29.96	3.28	1.36	0.34	0.59	0.35	1.033	0.169	0.021	0.235
865.0	28.54	6.98	2.33	0.45	1.31	1.47	4.321	0.229	0.069	0.190
877.0	29.88	5.62	1.43	0.32	0.81	1.30	3.100	0.210	0.032	0.127
887.0	29.55	5.77	1.92	0.38	0.86	1.22	2.896	0.239	0.040	0.145
897.0	29.59	5.40	1.56	0.46	0.80	0.80	2.314	0.271	0.029	0.154
906.0	29.14	7.17	1.74	0.43	1.01	1.59	4.179	0.267	0.038	0.135
915.0	29.21	5.80	2.22	0.54	0.73	0.55	1.674	0.347	0.018	0.180
924.5	28.10	6.71	2.16	0.64	0.76	0.61	1.925	0.378	0.023	0.195
932.5	28.60	7.26	2.17	0.49	0.63	2.33	3.188	0.292	0.091	0.131
941.0	28.90	5.25	2.85	0.57	0.68	0.39	1.227	0.341	0.024	0.178
951.0	28.20	6.46	2.06	0.58	0.75	0.79	1.897	0.389	0.031	0.182
961.0	29.17	6.32	1.94	0.63	0.69	0.55	1.502	0.413	0.019	0.185
977.0	29.18	7.30	2.26	0.74	0.80	0.50	1.560	0.469	0.018	0.227
987.0	29.03	5.84	1.89	0.68	0.72	0.49	1.478	0.376	0.017	0.165
997.0	27.95	7.38	2.20	0.75	0.89	0.60	1.852	0.434	0.019	0.216
1007.0	26.90	8.86	2.46	1.00	2.63	1.58	5.093	0.354	0.053	0.275
1017.0	28.12	7.75	2.30	0.86	2.02	1.27	3.960	0.341	0.041	0.204
1027.0	30.07	6.33	2.07	0.70	1.00	0.63	1.677	0.422	0.025	0.202
1037.0	30.06	6.56	2.15	0.67	0.83	0.50	1.417	0.422	0.050	0.196
1047.0	28.14	7.55	2.60	0.74	1.08	0.51	1.410	0.476	0.093	0.255
1057.0	28.90	6.14	2.72	0.67	0.78	0.43	1.317	0.421	0.075	0.192
1067.0	30.13	5.87	2.19	0.64	0.76	0.39	1.215	0.415	0.033	0.194
1077.0	30.65	5.82	2.11	0.64	0.80	0.39	1.195	0.414	0.051	0.194
1087.0	29.47	6.76	2.35	0.77	1.15	0.48	1.445	0.457	0.158	0.221
1097.0	25.56	9.63	3.30	1.24	2.35	0.87	2.608	0.581	0.175	0.285
1105.5	23.86	8.83	3.78	1.56	4.65	1.95	4.733	0.403	0.097	0.225
1112.0	25.61	9.09	3.28	1.16	3.95	2.16	5.274	0.355	0.100	0.193
1118.5	25.41	9.27	3.57	1.25	4.38	2.14	5.333	0.376	0.097	0.206
1127.0	29.86	5.58	3.47	0.86	1.41	0.51	1.419	0.361	0.444	0.158
1137.0	31.17	5.33	2.61	0.75	0.98	0.40	1.177	0.372	0.183	0.161
1147.0	31.91	5.45	2.34	0.72	0.84	0.40	1.117	0.377	0.095	0.163
1156.0	31.35	6.30	2.31	0.74	0.86	0.39	1.228	0.435	0.025	0.195
1161.0	30.49	6.83	2.57	0.75	1.22	0.75	1.636	0.469	0.033	0.216
1171.0	31.33	5.72	2.81	0.70	1.16	0.57	1.266	0.401	0.043	0.214
1181.0	31.94	4.28	3.25	0.61	0.81	0.29	0.862	0.301	0.093	0.233
1191.0	31.77	4.85	3.08	0.65	0.89	0.33	0.976	0.333	0.061	0.203
1201.0	29.16	6.97	3.14	0.98	1.50	0.51	1.461	0.485	0.040	0.247
1211.0	28.54	7.55	3.38	0.96	1.27	0.45	1.446	0.540	0.040	0.300
1221.0	27.46	8.38	3.72	1.00	1.21	0.49	1.536	0.592	0.049	0.332
1236.0	30.64	6.84	2.35	0.76	0.88	0.47	1.353	0.493	0.015	0.215
1246.0	27.48	8.99	2.94	0.87	1.03	0.50	1.534	0.631	0.023	0.299
1255.0	29.43	7.86	2.46	0.81	1.02	0.51	1.494	0.513	0.022	0.260
1264.0	29.70	7.38	2.57	0.80	1.02	0.53	1.514	0.501	0.026	0.264
1274.0	25.46	9.41	3.65	1.35	2.10	0.64	1.842	0.624	0.054	0.374
1281.0	29.73	7.56	3.24	0.92	1.12	0.52	1.513	0.506	0.056	0.255

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1288.0  28.20   7.75   3.43   0.91   1.35   0.65  1.797  0.493  0.057  0.277
1298.0  27.70   7.52   4.31   0.95   1.20   0.47  1.422  0.476  0.069  0.391
1308.0  26.82   8.88   3.69   0.88   1.31   0.46  1.296  0.496  0.041  0.353
1320.0  25.61  10.14   3.40   0.99   1.57   0.60  1.767  0.549  0.038  0.319
1327.0  29.98   6.66   3.13   0.92   1.45   0.55  1.634  0.420  0.029  0.219
1335.0  30.24   6.63   3.19   0.76   1.06   0.35  1.172  0.438  0.025  0.223
1344.0  27.25   6.99   5.63   0.73   1.29   0.54  1.415  0.454  0.234  0.251
1349.0  27.67   7.21   3.96   0.78   1.20   0.55  1.706  0.461  0.032  0.231
1359.0  28.02   5.21   4.26   0.60   0.91   0.37  1.077  0.327  0.020  0.244
1369.0  26.27   8.32   4.35   0.95   1.28   0.51  1.541  0.495  0.041  0.383
1379.0  24.90   7.13   6.62   0.86   1.24   0.40  1.309  0.447  0.383  0.451
1389.0  24.33   7.37   6.67   0.93   1.98   0.49  1.547  0.472  0.793  0.417
1398.0  24.81   8.88   4.58   1.00   2.60   0.80  2.260  0.543  0.293  0.327
1410.0  24.93   9.59   4.73   1.06   1.71   0.85  2.136  0.556  0.259  0.392
1420.0  24.39  11.18   3.90   1.14   1.84   0.81  2.315  0.649  0.074  0.316
1430.0  25.50  10.24   3.44   1.04   1.94   1.19  3.285  0.538  0.067  0.236
1438.5  27.15   9.34   2.64   0.54   1.71   2.27  6.115  0.286  0.090  0.087
1446.0  25.76   8.71   4.72   0.49   1.83   2.22  6.006  0.245  0.158  0.087
1453.0  27.45   9.21   2.47   0.49   1.75   2.39  6.445  0.250  0.094  0.060
1464.0  26.70   7.40   4.88   0.96   1.74   0.64  1.886  0.446  0.500  0.235
1475.0  24.01   8.08   4.99   1.08   3.72   0.53  1.652  0.543  0.596  0.318
1486.0  23.68   9.22   4.85   1.16   2.97   0.52  1.488  0.613  0.537  0.370
1496.5  24.42   9.78   4.83   1.14   2.23   0.49  1.531  0.664  0.287  0.404
1507.0  23.91   8.43   7.03   1.08   2.29   0.39  1.292  0.564  0.606  0.385
1517.0  22.75   8.34   8.85   0.97   2.01   0.41  1.260  0.551  0.491  0.352
1527.0  25.44   9.54   4.53   1.06   1.71   0.42  1.502  0.700  0.074  0.384
1537.0  24.96   9.30   5.14   1.03   1.87   0.43  1.426  0.666  0.186  0.365
1595.5  23.27   9.21   4.37   1.08   4.75   0.97  2.300  0.551  0.265  0.280
1605.5  23.40   9.81   4.84   1.25   3.88   0.91  2.242  0.622  0.191  0.343
1618.0  23.49   8.31   5.33   1.18   4.17   0.73  1.916  0.539  0.278  0.271
1627.0  22.87  10.59   4.22   1.29   3.20   0.68  1.767  0.744  0.093  0.399
1636.5  22.69   8.05   5.99   1.13   3.93   0.60  1.498  0.529  0.455  0.298
1645.5  22.09   7.40   4.24   1.58   9.03   1.28  2.906  0.390  0.169  0.181
1654.5  22.20   6.63   5.86   0.83   5.68   0.41  1.052  0.469  0.205  0.222
1664.5  22.21   7.33   4.28   0.91   6.27   0.46  1.147  0.534  0.205  0.255
1674.5  23.45   8.49   4.24   1.76   7.40   1.35  3.878  0.406  0.156  0.189
1685.0  19.96   5.59   6.01   0.71   6.21   0.32  0.804  0.411  2.722  0.262
1695.0  21.96   8.65   4.12   0.98   5.02   0.49  1.316  0.636  0.681  0.299
1704.0  16.20   3.76  10.01   0.55   7.38   0.20  0.560  0.349  3.856  0.265
1727.0  21.04   9.04   4.81   1.51   6.55   0.69  1.514  0.561  0.251  0.362
1746.0  22.78   4.75   8.98   0.73   3.12   0.36  0.933  0.354  0.857  0.328
1756.5  22.83   7.20   6.95   1.03   3.40   0.57  1.922  0.594  0.379  0.347
1765.5  19.35   4.56   9.03   0.70   7.13   0.35  0.699  0.269  1.014  0.300
1774.5  15.37   4.69  10.24   0.78   9.15   0.34  0.591  0.250  1.515  0.346
1783.5  14.19   1.48  11.47   0.37   9.53   0.11  0.238  0.094  1.476  0.378
1794.0  16.87   2.73   8.59   0.51   9.50   0.17  0.399  0.161  1.008  0.391
1804.5  16.49   1.33  12.78   0.30   7.95   0.11  0.230  0.101  1.881  0.217
1821.5  21.33   6.39   6.68   0.92   5.97   0.38  1.126  0.481  0.526  0.268
1832.0  23.97   7.71   6.66   0.99   2.40   0.41  1.316  0.633  0.328  0.303
1842.0  22.43   9.47   5.17   1.12   3.93   0.51  1.483  0.780  0.201  0.372
1851.0  21.72   8.82   5.45   1.21   4.99   0.52  1.566  0.650  0.371  0.350
1860.0  17.58   6.33   5.41   1.19  10.91   0.39  1.386  0.486  0.718  0.266
1869.0  16.51   6.13   4.66   1.20  12.63   0.39  1.377  0.450  0.841  0.250
1878.5  18.81   8.26   5.99   1.40   7.93   0.42  1.735  0.621  0.375  0.345
1888.0  16.77   7.80   8.29   1.34   8.62   0.48  1.634  0.534  0.457  0.323
1898.0  18.02   8.64   5.16   1.49   8.96   0.44  1.849  0.600  0.324  0.341
1909.0  19.33   9.83   5.25   1.61   6.96   0.52  1.961  0.639  0.182  0.383
1929.0  20.69   9.59   4.91   1.74   6.85   0.83  2.350  0.576  0.153  0.337
1940.5  19.14   9.52   6.18   1.72   6.67   0.53  2.099  0.623  0.177  0.373
1949.5  21.39  10.53   4.36   1.89   5.33   0.67  2.356  0.663  0.111  0.394
1959.0  21.42  10.03   5.29   1.88   5.40   0.79  2.654  0.620  0.126  0.361
1969.0  20.93  10.28   5.35   1.94   4.88   0.58  2.385  0.705  0.111  0.390
1979.0  20.51   9.86   6.45   1.94   5.23   0.62  2.291  0.667  0.153  0.384
1988.0  20.58   9.30   6.02   2.21   6.15   0.59  2.312  0.683  0.138  0.384
1997.5  20.73  10.06   5.81   1.95   5.00   0.62  2.366  0.672  0.124  0.384
2006.5  20.94  10.08   5.76   2.05   4.60   0.59  2.506  0.685  0.119  0.387
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2015.5  22.35   9.87   4.58   2.33   4.67   0.62  2.776  0.721  0.100  0.397
2026.0  21.91  10.03   5.08   2.22   4.30   0.59  2.758  0.710  0.107  0.394
2035.0  21.32   9.66   6.33   2.29   4.41   0.57  2.676  0.718  0.138  0.388
2044.0  21.68   9.86   5.79   2.37   4.41   0.57  2.809  0.732  0.131  0.394
2053.5  21.77   9.60   5.25   2.42   4.94   0.59  2.725  0.725  0.116  0.399
2064.0  21.04   9.68   5.27   2.45   4.93   0.54  2.795  0.712  0.134  0.382
2080.0  20.75   9.36   5.45   2.53   5.46   0.52  2.760  0.722  0.139  0.376
2096.0  21.26   9.27   4.96   2.49   5.59   0.55  2.841  0.689  0.134  0.379
2114.0  21.04   9.98   4.95   2.45   5.09   0.60  2.664  0.675  0.131  0.388
2239.5  22.39   7.72   5.34   2.70   6.29   0.59  2.801  0.629  0.132  0.295
2248.5  24.20   5.83   6.67   0.79   5.18   0.42  1.125  0.400  0.256  0.274
2258.0  31.87   3.85   5.20   0.36   0.86   0.60  1.075  0.212  0.143  0.196
2267.0  30.53   5.08   4.83   0.41   0.96   1.19  1.784  0.247  0.151  0.181
2276.0  28.95   5.40   5.29   0.74   1.94   0.50  1.146  0.345  0.181  0.243
2285.5  29.57   2.01  10.78   0.26   0.83   0.14  0.392  0.141  0.454  0.189
2294.5  29.23   2.24  10.73   0.28   0.85   0.13  0.428  0.155  0.427  0.186
2303.5  24.73   5.86   8.07   0.68   2.87   1.02  2.411  0.255  0.361  0.159
2313.0  29.99   5.63   4.23   0.62   1.50   0.56  1.302  0.358  0.263  0.231
2349.5  25.58   8.77   4.19   1.44   2.78   0.74  1.925  0.611  0.074  0.324
2360.0  24.50   8.55   5.12   1.22   3.09   0.61  1.711  0.618  0.133  0.324
2370.0  24.90   7.33   4.00   1.69   4.21   0.96  2.043  0.503  0.089  0.206
2379.0  25.70   8.07   4.54   1.28   2.72   0.66  1.759  0.584  0.089  0.258
2389.0  24.80   8.82   5.28   1.13   2.40   0.57  1.708  0.619  0.106  0.309
2399.0  25.30   8.88   4.81   1.17   2.40   0.61  1.854  0.618  0.094  0.323
2413.5  23.80   9.65   5.31   1.18   2.59   0.74  1.999  0.656  0.176  0.335
2423.0  23.84   9.68   5.20   1.19   2.69   0.82  2.050  0.661  0.155  0.326
2432.5  23.37  10.56   4.60   1.17   2.36   0.86  2.100  0.720  0.109  0.330
2445.5  24.86  10.28   3.47   1.04   2.07   1.55  3.001  0.578  0.084  0.210
2457.5  26.09   9.63   2.91   0.69   1.75   2.33  4.279  0.425  0.117  0.133
2470.0  27.13   9.52   2.62   0.59   2.05   3.34  5.514  0.289  0.125  0.063
2480.0  25.07   9.91   3.58   0.81   2.05   1.97  3.390  0.515  0.125  0.225
2490.0  25.40   9.68   3.79   0.84   1.91   1.78  3.083  0.527  0.127  0.217
2499.5  27.67   8.29   3.36   0.86   1.66   1.11  2.178  0.471  0.065  0.207
2508.5  28.23   6.34   5.54   0.63   1.51   0.97  1.815  0.331  0.142  0.178
2518.0  27.33   7.01   5.54   0.94   2.05   0.56  1.230  0.428  0.134  0.214
2527.0  27.85   7.52   3.86   1.02   2.21   0.57  1.397  0.475  0.084  0.224
2549.5  29.60   6.08   4.35   0.84   1.50   0.44  1.216  0.408  0.096  0.290
2561.0  27.35   6.63   5.66   0.82   1.96   0.86  1.723  0.367  0.201  0.257
2570.0  21.69   4.21  14.65   0.53   1.61   0.27  0.775  0.276  0.898  0.235
2579.0  27.74   7.30   4.30   1.01   2.18   0.37  1.207  0.474  0.220  0.322
2588.0  25.84   7.87   4.81   1.14   2.49   0.55  1.393  0.533  0.272  0.350
2609.5  22.74   9.57   6.09   1.19   2.63   0.53  1.524  0.615  0.769  0.427
2620.0  23.08   8.76   7.19   1.01   2.14   0.80  1.651  0.576  0.622  0.332
2631.5  25.36   9.51   3.97   0.92   1.96   1.60  2.486  0.539  0.160  0.292
2645.0  28.61   7.09   3.95   0.89   1.45   0.50  1.336  0.482  0.086  0.323
2654.0  26.47   8.64   4.01   1.03   2.14   1.04  2.083  0.519  0.127  0.326
2663.5  29.69   6.64   3.40   0.72   1.33   1.06  1.973  0.380  0.137  0.222
2672.5  22.26   4.34  13.21   0.50   1.74   0.58  1.054  0.257  1.185  0.237
2681.5  31.14   5.44   3.30   0.68   1.22   0.36  0.923  0.368  0.313  0.253
2690.5  29.68   5.88   3.83   0.77   1.56   0.41  0.959  0.387  0.427  0.330
2699.5  29.01   4.07   6.17   0.56   1.32   0.30  0.745  0.272  1.154  0.359
2708.0  27.25   4.38   7.62   0.75   1.70   0.39  0.863  0.317  1.242  0.354
2717.5  30.21   4.08   5.28   0.55   1.18   0.29  0.712  0.272  0.714  0.388
2729.0  31.29   4.57   3.24   0.62   1.24   0.28  0.759  0.301  0.105  0.393
2748.0  31.48   4.44   3.02   0.72   1.36   0.28  0.731  0.291  0.091  0.365
2826.5  28.76   5.79   4.02   0.92   2.15   0.44  1.009  0.385  0.136  0.325
2855.5  30.67   5.85   2.85   0.53   1.25   1.04  1.930  0.297  0.101  0.351
2874.0  32.19   4.58   2.81   0.77   1.62   0.40  1.031  0.298  0.077  0.297
2883.0  26.12   2.72  11.62   0.34   1.22   0.15  0.454  0.181  0.789  0.236
2892.5  32.46   4.95   2.28   0.52   0.85   0.29  0.812  0.311  0.055  0.180
2902.0  29.99   6.37   2.81   0.57   1.12   0.85  1.562  0.355  0.072  0.208
2911.0  30.33   6.22   2.79   0.69   1.17   0.73  1.491  0.353  0.159  0.186
2920.5  25.87   8.82   3.66   1.19   2.50   0.60  1.297  0.506  0.062  0.298
2930.5  28.36   7.16   3.61   0.90   1.42   0.47  1.268  0.465  0.152  0.238
2952.5  25.68   9.04   3.94   1.09   2.15   0.59  1.312  0.525  0.079  0.340
2964.0  29.27   6.67   3.42   0.79   1.26   0.69  1.489  0.399  0.128  0.232
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2976.5  32.02   4.88   3.15   0.57   0.96   0.58  1.224  0.284  0.075  0.198
2989.5  31.71   4.45   3.67   0.51   0.94   0.29  0.774  0.268  0.187  0.238
3000.0  31.51   4.15   4.22   0.54   1.08   0.30  0.737  0.272  0.248  0.235
3011.5  33.71   3.32   3.19   0.40   0.73   0.20  0.556  0.205  0.207  0.212
3021.5  34.95   2.63   2.81   0.35   0.58   0.17  0.466  0.172  0.242  0.166
3031.5  35.38   2.21   2.95   0.29   0.58   0.16  0.445  0.136  0.342  0.141
3044.5  34.59   1.48   3.58   0.24   1.34   0.09  0.275  0.095  0.508  0.121
3056.0  28.41   1.92   7.40   0.29   3.83   0.11  0.329  0.117  0.494  0.222
3067.5  28.29   1.74  11.01   0.26   0.98   0.12  0.320  0.115  0.503  0.195
3078.0  32.56   3.79   3.37   0.44   0.73   0.21  0.615  0.229  0.109  0.225
3088.0  28.17   5.42   6.10   0.65   1.22   0.31  0.931  0.332  0.220  0.225
3098.5  26.49   7.00   5.59   0.91   1.69   0.47  1.218  0.436  0.193  0.250
3110.0  27.71   7.50   3.75   1.01   1.64   0.60  1.424  0.465  0.061  0.224
3122.0  27.19   8.25   3.78   1.03   1.49   0.53  1.462  0.542  0.066  0.249
3155.5  28.62   6.83   3.63   0.93   1.55   0.55  1.349  0.450  0.078  0.275
3166.0  29.30   6.71   3.13   0.63   1.27   1.06  1.870  0.349  0.102  0.255
3176.5  30.40   5.70   3.25   0.59   0.98   0.36  0.948  0.363  0.087  0.267
3187.0  29.99   4.58   5.23   0.52   1.02   0.28  0.787  0.300  0.214  0.271
3197.0  27.58   3.33   9.20   0.44   1.28   0.23  0.596  0.223  0.370  0.288
3207.0  32.31   4.44   3.00   0.53   0.98   0.33  0.862  0.273  0.132  0.351
3217.5  29.69   6.50   2.99   0.71   1.20   0.40  1.121  0.406  0.093  0.339
3226.5  28.98   6.92   3.05   0.71   1.24   0.41  1.090  0.396  0.095  0.326
3236.5  31.23   5.22   2.90   0.58   1.11   0.37  1.058  0.308  0.107  0.339
3249.5  31.91   4.47   3.31   0.50   0.80   0.26  0.743  0.288  0.104  0.280
3258.5  29.39   4.89   5.16   0.63   1.27   0.34  0.861  0.330  0.315  0.317
3268.0  31.92   4.55   3.02   0.52   0.93   0.29  0.752  0.298  0.134  0.444
3277.0  31.37   4.90   2.90   0.56   1.07   0.38  0.920  0.355  0.141  0.441
3286.5  31.33   4.32   3.09   0.97   1.95   0.60  1.229  0.311  0.144  0.399
3297.5  30.28   5.75   2.72   0.59   1.54   0.88  1.756  0.255  0.121  0.338
3307.5  33.01   3.34   2.80   0.44   0.93   0.24  0.488  0.194  0.181  0.517
3317.0  35.37   1.85   2.55   0.27   0.42   0.16  0.357  0.118  0.190  0.508
3326.0  33.63   3.23   2.59   0.41   0.78   0.42  0.890  0.193  0.133  0.395
3337.0  34.53   2.59   2.57   0.35   0.59   0.22  0.530  0.160  0.162  0.409
3356.5  35.81   1.63   2.70   0.23   0.42   0.12  0.290  0.105  0.194  0.506
3367.0  34.95   1.86   3.53   0.26   0.54   0.12  0.342  0.127  0.202  0.443
3378.5  31.84   3.71   3.58   0.51   1.17   0.27  0.615  0.217  0.171  0.373
3390.0  34.42   1.78   3.60   0.22   0.47   0.23  0.493  0.102  0.243  0.512
3402.5  35.06   1.42   3.88   0.20   0.41   0.09  0.229  0.090  0.190  0.549
3412.0  34.11   1.98   2.89   0.30   0.64   0.43  0.396  0.135  0.180  0.429
3422.5  33.31   2.56   3.11   0.35   0.75   0.19  0.527  0.172  0.184  0.508
3433.5  32.55   3.13   3.11   0.56   1.13   0.26  0.585  0.211  0.198  0.508
3444.0  31.10   4.69   3.52   0.45   0.94   0.59  1.276  0.276  0.181  0.432
3454.0  28.16   6.69   4.22   0.81   1.58   0.40  1.100  0.482  0.133  0.415
3464.0  28.41   5.44   5.21   0.67   1.59   0.28  0.774  0.353  0.284  0.403
3474.5  28.55   6.29   3.85   0.78   1.39   0.36  1.012  0.400  0.130  0.411
3485.0  27.79   6.80   3.59   0.88   2.04   0.45  0.967  0.413  0.128  0.427
3495.5  29.42   6.09   3.47   0.81   1.42   0.45  1.066  0.382  0.123  0.377
3504.5  28.05   6.49   4.20   0.87   1.46   0.46  1.239  0.413  0.145  0.445
3514.5  27.82   6.76   4.46   0.85   1.56   0.55  1.371  0.411  0.174  0.397
3524.5  26.12   8.06   4.65   0.87   1.80   1.20  2.304  0.422  0.198  0.334
3534.0  25.37   7.83   5.36   1.01   2.09   0.43  1.224  0.470  0.222  0.458
3543.0  27.01   7.20   4.16   1.11   2.15   0.51  1.177  0.452  0.112  0.386
3561.0  28.64   5.95   4.16   0.80   1.40   0.37  1.040  0.380  0.124  0.483
3571.5  29.41   5.86   3.57   0.74   1.52   0.38  0.949  0.342  0.134  0.445
3581.5  32.02   4.14   3.47   0.52   0.98   0.24  0.694  0.276  0.162  0.430
3591.0  27.79   7.42   3.76   0.95   2.20   0.41  1.093  0.435  0.117  0.457
3600.0  27.13   7.72   3.96   1.01   2.18   0.99  1.872  0.445  0.130  0.353
3609.0  26.93   7.49   4.51   0.99   1.79   0.66  1.499  0.484  0.167  0.360
3619.5  26.35   7.67   5.13   1.00   1.85   0.55  1.390  0.483  0.200  0.394
3630.0  26.80   7.54   4.65   1.00   1.77   0.60  1.426  0.475  0.170  0.387
3642.0  27.64   6.94   4.50   0.87   1.43   0.59  1.418  0.441  0.172  0.345
3666.0  26.19   7.91   4.50   1.03   2.39   0.46  1.126  0.499  0.138  0.524
3677.5  26.20   7.81   5.33   0.88   1.93   0.44  1.098  0.473  0.188  0.445
3705.5  28.04   7.95   3.55   0.83   1.68   0.91  1.800  0.428  0.097  0.330
3717.0  27.58   7.62   3.82   0.95   1.98   0.69  1.359  0.460  0.153  0.324
3727.5  25.21   8.06   5.08   1.61   3.48   0.77  1.384  0.565  0.174  0.382
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3738.0  28.36   7.16   3.75   0.81   1.57   0.51  1.124  0.429  0.092  0.403
3768.0  26.28   9.01   3.64   1.05   2.25   1.12  1.819  0.499  0.092  0.299
3779.5  26.09   8.59   3.92   1.23   2.75   1.30  1.988  0.524  0.119  0.327
3790.0  27.51   8.11   3.41   0.80   1.62   1.08  1.815  0.453  0.114  0.326
3800.0  27.33   7.96   3.74   0.84   1.60   0.70  1.460  0.465  0.099  0.386
3810.5  27.39   7.71   3.84   0.85   1.65   0.60  1.357  0.470  0.079  0.384
3854.0  28.00   6.91   4.21   0.84   1.79   0.43  1.098  0.426  0.189  0.365
3864.0  23.92   9.83   4.79   1.38   3.10   0.84  1.715  0.591  0.147  0.390
3876.0  23.88   9.46   5.21   1.45   3.09   0.58  1.450  0.655  0.157  0.409
3886.0  25.61   8.46   4.73   1.21   2.52   0.52  1.396  0.567  0.159  0.407
3896.5  23.28   9.86   4.83   1.67   4.13   0.74  1.404  0.645  0.111  0.463
3908.5  23.92   9.62   5.08   1.37   2.89   0.54  1.468  0.673  0.121  0.411
3919.5  23.97   9.66   4.99   1.36   2.72   0.58  1.560  0.664  0.123  0.403
3938.5  23.37   9.57   5.79   1.17   2.60   1.10  1.957  0.613  0.202  0.359
3948.0  24.14   9.53   5.03   1.19   2.52   0.45  1.385  0.658  0.120  0.443
3957.0  23.45  10.47   4.96   1.32   2.76   0.53  1.466  0.730  0.110  0.452
3967.0  24.53   9.92   4.78   1.15   2.34   0.38  1.383  0.664  0.110  0.436
3977.5  23.56  10.53   5.14   1.18   2.37   0.42  1.358  0.681  0.131  0.401
3988.0  21.26  10.37   7.56   1.20   2.81   0.41  1.400  0.712  0.299  0.452
3998.0  21.10  10.53   7.76   1.18   2.73   0.43  1.346  0.704  0.292  0.435
4008.5  22.42  11.46   5.12   1.32   2.96   0.47  1.468  0.786  0.129  0.458
4017.5  22.96  11.32   4.64   1.23   2.72   0.50  1.371  0.748  0.090  0.424
4029.0  22.37  10.84   5.69   1.40   3.22   0.52  1.442  0.755  0.174  0.460
4052.0  23.44   9.78   5.58   1.30   2.92   0.47  1.452  0.683  0.174  0.423
4062.5  22.03   8.49   8.49   1.16   2.86   0.49  1.365  0.567  0.343  0.374
4073.0  24.81   9.02   4.81   1.35   3.07   0.74  1.828  0.614  0.169  0.348
4083.5  25.34   9.20   4.20   1.24   2.60   0.92  1.857  0.621  0.093  0.399
4097.0  22.89   9.58   6.20   1.30   3.02   0.43  1.379  0.656  0.258  0.433
4106.5  23.59   8.53   6.47   1.16   2.58   0.43  1.340  0.583  0.313  0.389
4120.0  25.14   8.59   4.35   1.35   2.93   0.91  1.815  0.591  0.105  0.320
4130.5  25.89   8.51   4.26   1.11   2.24   0.87  1.779  0.548  0.111  0.380
4139.5  25.46   8.39   4.87   1.22   2.49   0.43  1.407  0.571  0.112  0.394
4149.0  22.91   8.04   7.02   1.27   3.30   0.44  1.363  0.578  0.227  0.350
4158.0  24.59   9.40   4.76   1.40   2.87   0.48  1.485  0.645  0.086  0.414
4167.5  24.98   9.31   4.46   1.34   2.66   0.46  1.527  0.639  0.073  0.434
4176.5  24.36  10.01   4.51   1.42   2.71   0.52  1.541  0.692  0.067  0.402
4185.5  20.54   8.76   9.34   1.28   3.34   0.48  1.340  0.621  0.292  0.387
4210.0  24.43   9.56   4.54   1.62   3.44   0.47  1.576  0.706  0.064  0.387
4220.5  24.62   9.00   4.58   1.63   3.95   0.60  1.518  0.639  0.086  0.381
4231.0  21.09   5.89  12.15   0.91   2.85   0.28  1.100  0.442  0.466  0.287
4241.0  24.90   8.11   4.81   1.23   3.38   0.41  1.443  0.637  0.120  0.340
4251.5  25.65   8.24   4.30   1.94   3.60   0.99  1.499  0.679  0.058  0.348
4262.0  26.46   8.78   3.86   1.15   2.23   0.44  1.528  0.627  0.046  0.312
4272.5  27.62   7.40   4.10   1.02   2.18   0.41  1.410  0.520  0.264  0.273
4281.5  23.61   9.13   6.30   1.33   2.63   0.46  1.517  0.694  0.205  0.394
4290.5  26.07   8.98   4.24   1.12   1.83   0.47  1.621  0.637  0.086  0.415
4303.5  24.22   8.57   5.78   1.75   3.42   0.46  1.592  0.727  0.146  0.407
4312.5  25.65   8.29   4.81   1.55   2.62   0.46  1.531  0.686  0.108  0.393
4323.0  24.46   9.79   4.53   1.42   2.77   0.47  1.624  0.783  0.081  0.431
4333.0  24.87   9.45   4.30   1.42   2.72   0.50  1.686  0.669  0.072  0.405
4342.0  25.76   8.70   4.51   1.28   2.36   0.59  1.782  0.618  0.100  0.329
4351.0  19.32   6.85  13.27   1.42   3.36   0.48  1.389  0.531  0.433  0.349
4361.0  26.27   8.86   4.01   1.13   2.05   0.72  2.187  0.561  0.078  0.372
4371.0  26.49   8.40   4.26   1.20   2.00   0.42  1.508  0.570  0.081  0.440
4380.0  28.53   7.15   3.81   0.98   1.51   0.42  1.390  0.475  0.074  0.399
4390.0  28.49   6.94   3.84   0.99   1.67   0.41  1.353  0.467  0.087  0.422
4412.0  25.12   9.05   4.29   1.25   2.58   0.47  1.491  0.626  0.056  0.455
4421.0  27.01   8.17   3.94   0.98   1.87   0.55  1.529  0.553  0.091  0.321
4437.5  26.18   8.86   4.04   1.13   2.26   0.44  1.401  0.592  0.077  0.419
4446.5  26.45   8.73   3.97   1.13   2.09   0.48  1.492  0.591  0.063  0.387
4456.0  26.68   8.46   3.94   1.09   2.19   0.82  2.213  0.519  0.096  0.334
4465.0  27.63   7.62   4.42   0.95   1.60   0.46  1.348  0.510  0.122  0.393
4473.5  27.21   7.92   4.39   0.95   1.59   0.53  1.531  0.504  0.115  0.415
4486.0  26.18   8.20   4.48   1.63   2.65   0.49  1.533  0.605  0.077  0.407
4496.0  27.15   8.23   3.88   1.11   1.81   0.49  1.508  0.581  0.069  0.357
4509.5  27.76   8.13   3.46   0.92   1.56   0.45  1.434  0.548  0.045  0.360
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4519.0  26.99   8.61   3.46   0.96   1.57   0.54  1.567  0.598  0.060  0.283
4528.0  24.27   8.20   6.74   0.97   1.96   0.54  1.525  0.572  0.234  0.307
4548.0  26.17   8.04   4.05   2.01   3.22   0.48  1.531  0.635  0.056  0.333
4556.0  25.49   9.03   4.18   1.20   2.03   0.47  1.573  0.649  0.080  0.362
4564.0  26.35   9.07   3.84   1.08   1.78   0.49  1.604  0.585  0.066  0.363
4577.0  23.99   8.96   5.43   2.23   4.02   0.62  1.621  0.717  0.113  0.358
4588.0  24.96   8.34   6.02   1.28   2.31   0.65  1.860  0.546  0.154  0.343
4597.5  23.73   8.67   6.94   1.23   2.20   0.50  1.609  0.590  0.172  0.357
4607.0  24.68  10.18   4.25   1.30   2.22   0.55  1.646  0.733  0.058  0.393
4618.0  26.30   9.09   3.81   1.09   1.87   0.68  1.660  0.573  0.074  0.338
4630.5  28.69   7.21   3.61   1.11   1.71   0.42  1.326  0.487  0.062  0.310
4641.0  28.15   7.92   3.44   1.02   1.66   0.45  1.383  0.502  0.053  0.297
4651.0  28.11   7.51   4.06   0.92   1.48   0.41  1.295  0.484  0.080  0.297
4661.0  25.38   6.94   6.38   2.08   3.76   0.47  1.342  0.558  0.153  0.311
4671.5  30.65   6.18   2.94   0.80   1.23   0.32  1.118  0.407  0.044  0.295
4681.5  27.51   8.55   3.59   0.98   1.54   0.44  1.448  0.530  0.062  0.371
4691.5  25.25   8.95   4.37   1.85   3.17   0.63  1.688  0.756  0.088  0.354
4710.0  26.43   8.22   3.87   1.32   2.52   0.51  1.415  0.562  0.061  0.355
4718.5  29.54   6.99   3.24   0.85   1.38   0.30  1.277  0.459  0.063  0.356
4730.0  28.75   7.32   3.24   1.01   1.86   0.38  1.335  0.473  0.051  0.347
4740.0  27.16   7.90   3.84   1.02   2.11   0.44  1.470  0.497  0.088  0.373
4751.5  28.18   7.56   3.34   0.79   1.75   1.19  2.468  0.403  0.127  0.249
4763.0  29.22   7.45   2.83   0.67   1.44   1.28  2.611  0.373  0.080  0.232
4773.0  27.26   8.50   3.43   0.95   1.62   0.46  1.456  0.629  0.060  0.313
4822.5  23.68  10.59   4.13   1.58   3.52   0.45  1.398  0.648  0.065  0.407
4839.0  24.63   9.62   4.26   1.83   3.41   0.49  1.535  0.658  0.058  0.383
4849.5  25.37   9.82   3.97   1.17   2.30   0.44  1.490  0.610  0.060  0.394
4859.5  27.10   8.37   3.35   0.98   2.07   0.46  1.416  0.501  0.049  0.337
4870.0  31.68   5.35   2.68   0.61   1.10   0.20  0.869  0.372  0.033  0.287
4880.0  30.12   6.17   2.64   0.69   1.72   0.30  0.835  0.348  0.063  0.283
4893.0  30.61   4.81   3.09   0.93   2.05   0.24  0.764  0.330  0.067  0.266
4902.5  30.30   3.78   5.12   0.48   1.06   0.18  0.685  0.253  0.360  0.259
4913.0  31.09   3.95   4.48   0.60   1.42   0.24  0.659  0.238  0.285  0.267
4923.5  34.72   2.43   3.02   0.29   0.65   0.13  0.440  0.138  0.294  0.220
4933.0  29.97   3.42   6.90   0.41   1.04   0.15  0.607  0.200  0.310  0.246
4943.0  29.72   5.89   3.25   0.73   1.72   0.32  0.928  0.343  0.332  0.273
4953.5  29.48   6.33   3.49   0.67   1.41   0.23  0.883  0.352  0.146  0.297
4962.5  22.42   6.99  10.34   0.77   1.69   0.32  1.056  0.413  0.451  0.310
4971.5  25.46   9.73   3.79   0.87   1.36   0.52  1.551  0.578  0.096  0.280
5006.5  27.27   8.03   3.72   0.99   1.78   0.40  1.395  0.515  0.057  0.324
5015.5  24.25   7.84   6.81   1.66   2.97   0.48  1.424  0.577  0.154  0.334
5025.0  25.49   9.10   3.94   1.20   2.46   0.49  1.558  0.563  0.068  0.351
5034.0  24.56   9.16   5.33   1.15   2.29   0.46  1.597  0.565  0.093  0.360
5043.0  22.96  10.21   5.86   1.20   2.47   0.61  1.778  0.652  0.125  0.375
5052.0  22.79  10.93   5.12   1.19   2.45   0.62  1.759  0.696  0.091  0.406
5061.0  23.06  11.01   4.76   1.07   2.59   1.15  2.691  0.602  0.115  0.349
5070.0  21.92  12.02   4.72   1.24   2.74   0.63  1.436  0.744  0.092  0.429
5079.0  22.36  11.05   4.44   1.46   3.33   0.61  1.440  0.701  0.089  0.410
5089.0  21.79   8.61   9.08   1.00   2.24   0.39  1.414  0.565  0.218  0.354
```

depth	Sc	Ba	V	La	Ce	Nd	Cr	Ni	Cu	Zn
5.0	11.8	1132.1	167.0	40.5	71.5	36.1	55.7	23.1	31.7	51.4
15.0	1.1	233.7	102.5	13.7	20.7	11.9	13.0	7.8	4.8	25.4
25.0	1.1	286.3	85.0	12.7	26.6	11.1	11.7	7.7	6.7	21.8
35.0	1.2	260.7	70.7	15.1	25.9	13.8	11.6	6.2	7.5	22.8
45.0	-0.1	167.5	85.7	13.9	22.0	14.4	8.5	5.2	5.0	16.6
55.0	3.6	111.5	97.4	4.5	6.5	5.2	10.8	3.3	6.6	8.8
65.0	3.4	108.6	97.1	5.8	3.8	4.1	8.6	3.3	10.5	10.6
75.0	3.9	160.1	74.6	7.4	9.9	6.3	11.5	5.0	14.6	15.4
85.0	2.7	106.7	85.8	11.4	5.1	5.6	8.8	4.7	7.0	15.3
95.0	-0.9	63.3	87.5	8.5	9.0	5.7	4.0	5.3	2.9	22.6
105.0	6.0	840.6	123.1	36.0	49.7	25.3	28.7	12.7	29.5	36.9
115.0	14.0	1818.6	168.0	67.6	100.5	46.4	63.5	21.7	38.2	71.7
125.0	3.9	265.3	109.8	12.1	18.2	12.0	26.3	8.2	7.0	15.4
135.0	3.7	42.0	115.5	4.8	6.7	7.1	10.1	3.4	2.7	12.1
145.0	3.8	61.3	104.4	6.2	2.3	5.7	7.9	3.0	3.2	11.4
155.0	1.3	53.9	99.3	6.5	1.0	6.0	10.1	3.0	2.6	12.6
165.0	3.9	65.4	100.3	5.5	8.3	3.7	10.6	4.3	4.2	15.3
183.0	1.5	81.5	101.4	21.5	18.6	8.2	13.3	6.2	4.2	19.9
193.0	1.4	86.1	97.5	20.0	12.5	6.7	12.2	7.8	2.7	21.5
203.0	1.3	71.4	75.4	2.2	20.1	12.0	9.7	5.3	2.6	18.0
213.0	-1.9	77.9	78.6	12.4	10.4	10.6	8.8	5.9	3.4	17.5
223.0	1.7	131.0	89.5	13.0	26.5	13.5	14.8	7.8	4.9	23.3
233.0	-0.6	166.9	110.5	15.8	37.4	13.4	16.3	8.6	4.8	27.8
243.0	3.0	120.1	89.9	20.1	42.5	13.8	12.9	7.8	4.8	31.2
253.0	2.6	110.9	102.2	17.6	26.1	7.8	14.2	6.8	3.3	23.0
263.0	1.4	94.9	114.4	8.6	13.5	7.0	11.9	7.7	3.0	29.3
273.0	-0.4	63.7	165.0	31.7	0.4	3.2	271.5	10.0	1.7	39.8
283.0	-0.1	69.0	167.1	15.0	15.2	5.8	76.4	6.9	0.7	43.5
293.0	2.3	77.3	142.4	5.3	16.4	7.6	52.8	5.9	3.7	37.4
303.0	3.2	139.3	152.5	9.2	21.9	8.7	64.0	6.4	4.9	37.0
310.5	3.6	888.8	156.8	48.4	76.1	30.1	106.8	10.5	17.8	67.1
315.5	5.2	1722.6	159.8	83.5	143.4	65.5	26.7	12.7	33.1	84.8
320.5	8.2	1513.1	154.6	84.4	151.9	50.5	44.2	17.5	33.5	81.7
327.5	0.9	344.3	127.7	26.9	42.8	23.2	55.4	6.6	8.2	38.6
335.5	1.5	1479.2	133.5	85.7	161.9	53.5	42.4	21.1	35.4	80.0
343.0	5.0	127.6	194.7	30.6	35.2	13.0	33.8	6.8	2.1	35.3
353.0	0.1	393.1	126.5	54.9	58.1	19.8	48.6	9.0	6.1	50.4
362.5	1.9	172.6	189.5	68.2	33.7	18.0	21.6	7.1	-1.3	41.8
377.0	5.6	747.9	161.9	60.7	85.6	34.1	22.5	10.2	10.7	256.2
387.0	2.2	222.6	233.0	23.7	36.8	17.5	22.7	10.3	2.8	312.7
397.0	3.2	137.2	182.9	13.6	19.2	8.5	24.0	10.6	1.3	405.4
407.0	1.9	148.7	194.2	15.7	31.0	13.3	17.7	9.5	2.4	388.1
417.0	2.9	125.0	248.9	12.7	22.2	7.7	20.8	9.6	0.0	348.4
427.0	4.5	351.2	207.8	22.4	37.9	16.1	15.9	7.6	1.5	180.6
437.0	2.0	115.2	189.8	18.0	19.9	7.9	14.2	6.5	2.4	215.3
447.0	3.3	800.6	136.3	33.1	61.4	26.4	11.0	6.9	4.1	163.6
457.0	0.5	90.0	257.3	14.1	14.5	6.3	14.7	8.2	-4.2	160.1
467.0	1.8	84.3	254.8	19.0	8.5	7.4	14.8	5.2	-4.7	192.8
477.0	-0.5	206.5	208.9	11.8	15.9	8.0	11.4	5.3	-6.6	156.5
487.0	1.1	76.7	258.2	7.5	6.8	3.6	14.7	5.3	-2.8	200.3
497.0	0.9	81.4	272.4	11.2	7.5	4.7	16.6	5.4	-2.6	206.6
507.0	3.6	213.3	206.4	48.2	88.4	28.6	15.0	5.7	-3.9	122.6
517.0	-2.3	75.9	310.1	6.1	11.0	6.2	17.0	5.4	-0.7	171.8
527.0	1.1	59.7	225.5	12.6	8.8	0.9	13.9	6.6	-0.1	146.5
537.0	2.1	40.4	140.1	12.1	10.5	9.6	12.1	3.3	6.4	134.8
547.0	0.8	51.8	231.7	14.4	3.2	4.2	16.3	2.6	5.5	114.6
555.0	0.9	51.1	291.1	5.8	9.7	2.4	18.0	5.0	6.1	120.2
562.0	-0.4	67.6	330.8	8.4	5.0	-0.1	17.1	5.9	5.4	99.0
577.0	0.5	263.5	206.3	12.0	28.8	4.8	13.5	10.5	10.7	248.8
587.0	1.6	227.6	240.9	6.4	13.4	5.1	14.5	8.6	5.1	198.8
597.0	-1.0	417.3	260.5	-2.6	16.1	8.9	14.7	15.4	2.4	235.1
607.0	-0.5	1814.9	268.2	5.1	5.0	9.9	15.7	18.5	6.1	136.8
617.0	-1.3	2530.7	261.1	11.7	26.4	10.7	16.1	18.1	12.7	122.8
626.0	3.7	2725.0	173.7	60.3	99.7	35.7	21.3	13.9	16.6	112.1
634.0	2.2	3948.7	253.6	26.5	52.2	20.9	18.8	14.0	9.8	212.3
642.0	3.1	2603.6	164.6	55.2	114.9	35.7	21.1	12.6	13.5	168.7
649.5	2.5	892.6	69.2	91.1	169.7	49.1	19.7	9.6	16.7	151.2
657.5	1.7	878.0	90.2	71.0	123.6	31.2	24.6	12.9	13.8	145.5
667.0	0.9	1885.5	143.1	27.0	48.0	19.4	8.1	12.8	4.2	118.7
677.0	0.9	1705.4	115.5	35.0	76.6	31.9	7.5	7.9	3.8	105.6
687.0	-0.8	286.7	228.7	8.5	12.9	7.6	11.7	15.6	-5.0	79.6
697.0	-1.8	155.3	274.5	-1.7	2.5	5.5	14.0	9.8	0.4	65.0
707.0	0.0	140.9	240.8	14.7	18.1	2.0	13.1	11.1	4.5	52.5
717.0	1.1	390.7	234.4	15.1	8.2	7.2	14.6	8.7	6.4	69.8
727.0	1.0	370.0	231.1	4.8	8.6	3.6	14.5	7.9	6.7	86.3
737.0	-0.6	293.6	214.5	4.5	9.9	4.5	14.8	7.6	4.6	74.2
747.0	0.4	1163.7	153.4	26.9	63.0	29.5	14.6	7.8	6.9	87.0
756.5	4.0	984.2	150.8	60.8	127.2	39.3	20.9	10.0	14.7	72.0
776.5	2.2	1111.0	123.4	48.6	101.5	41.7	27.3	13.8	17.3	70.9
785.0	5.1	2037.2	122.0	66.8	132.8	54.8	24.1	8.5	14.6	82.4
794.0	0.2	556.2	144.5	32.7	88.3	27.6	34.6	19.7	16.0	59.1
804.0	4.2	848.9	181.3	30.4	83.3	37.4	38.2	22.6	17.2	63.5
814.5	4.1	1539.4	231.5	34.5	80.2	29.3	35.1	20.1	13.1	58.1
825.0	1.4	580.1	339.0	23.7	36.5	21.3	32.4	27.7	11.2	56.5
835.0	4.4	344.0	350.9	21.5	52.9	19.9	35.9	33.1	13.4	56.1
845.0	4.2	321.6	267.9	26.3	65.0	26.9	31.0	18.6	10.2	55.7
855.0	7.6	608.0	221.1	47.5	92.8	33.4	31.1	17.2	15.6	56.2
865.0	5.9	959.9	141.4	65.9	147.2	55.6	19.1	9.9	9.9	73.0
877.0	4.2	391.8	144.3	53.1	133.9	42.7	32.3	13.4	12.3	65.7
887.0	5.5	458.9	136.5	70.0	154.8	54.4	28.4	15.4	11.3	66.1
897.0	7.4	547.3	156.3	72.0	143.6	49.5	43.8	16.2	18.0	60.6
906.0	5.4	683.7	113.7	68.0	141.9	44.8	128.4	26.2	11.9	72.7
915.0	7.6	580.6	170.7	90.5	185.2	62.3	54.3	28.6	27.0	77.6
924.5	9.0	689.1	174.9	98.6	173.4	57.5	60.6	27.9	31.6	90.6
932.5	5.1	523.2	94.6	123.0	242.3	68.4	24.7	12.8	12.3	106.2
941.0	6.6	584.0	184.6	84.8	173.3	59.6	60.0	29.8	33.4	68.7
951.0	7.2	665.8	242.7	113.9	231.2	70.4	64.5	27.7	32.7	86.8
961.0	10.6	612.2	205.2	109.8	216.9	73.2	72.4	30.6	37.5	74.7
977.0	15.6	816.1	219.5	129.5	233.0	80.0	87.0	41.2	43.6	216.4
987.0	11.6	590.1	241.8	85.0	189.4	62.3	80.9	34.9	33.6	157.5
997.0	10.1	825.4	231.0	110.5	236.3	80.3	80.2	35.5	43.9	189.9
1007.0	7.2	1328.3	131.2	76.3	153.7	54.5	39.6	20.2	32.8	162.2
1017.0	5.2	1033.2	142.6	79.6	149.4	54.7	53.5	23.8	28.4	175.6
1027.0	10.5	785.4	186.2	105.2	217.6	76.6	67.5	34.7	36.6	246.9
1037.0	8.4	784.4	176.5	123.3	244.5	77.4	71.1	39.8	40.9	220.8
1047.0	11.2	1026.1	202.7	141.0	278.2	92.8	69.4	44.7	47.9	229.4
1057.0	9.7	727.1	206.4	119.4	214.3	74.0	75.6	41.0	42.1	194.7
1067.0	11.2	729.1	207.1	113.7	217.6	71.2	73.8	39.8	40.2	197.1
1077.0	9.3	744.3	189.8	117.5	215.1	72.1	69.4	37.1	40.4	173.6
1087.0	11.8	932.1	181.2	127.6	237.9	78.4	69.5	37.8	45.6	201.4
1097.0	14.5	1372.4	205.5	153.5	283.8	97.1	84.9	43.7	49.9	184.2
1105.5	7.3	1764.0	146.4	63.3	150.0	53.8	43.4	19.5	28.5	132.5
1112.0	5.9	1563.0	113.7	60.7	138.0	54.5	34.0	15.0	23.4	158.2
1118.5	6.1	1751.4	124.9	58.3	131.5	51.6	30.3	11.5	23.5	126.5
1127.0	10.1	700.3	178.1	96.5	162.2	57.9	72.1	43.7	32.8	208.5
1137.0	12.0	748.5	196.9	82.2	169.4	56.6	74.0	45.8	37.3	174.1
1147.0	10.2	719.7	200.0	93.6	165.8	59.4	79.9	51.8	33.4	148.3
1156.0	9.8	841.4	233.9	114.2	210.1	75.6	92.4	55.6	40.4	129.0
1161.0	11.7	1038.6	206.3	119.0	207.4	75.6	70.0	51.7	39.1	99.3
1171.0	9.8	841.8	201.4	105.6	173.6	66.2	71.0	45.0	38.2	107.8
1181.0	8.9	602.9	193.4	81.1	127.2	53.2	61.3	42.1	35.3	104.6
1191.0	9.1	700.9	189.0	96.6	150.3	58.7	62.7	43.8	38.4	113.8
1201.0	10.9	1057.8	194.6	133.9	218.9	80.4	87.1	57.7	50.4	121.8
1211.0	13.8	1152.1	225.1	151.3	262.3	93.8	97.1	63.4	60.8	125.7
1221.0	15.9	1224.9	246.7	167.6	283.0	108.0	102.4	71.1	63.6	132.8
1236.0	15.0	960.8	212.8	137.7	229.9	87.4	88.4	44.3	53.1	100.3
1246.0	16.5	1428.7	243.5	185.3	319.3	115.7	109.8	63.3	66.9	121.8
1255.0	12.9	1174.2	212.5	158.3	252.5	94.3	83.0	38.8	62.3	110.3
1264.0	11.9	1241.3	221.6	146.2	244.1	92.0	82.6	48.2	57.6	106.1
1274.0	16.1	1207.5	233.5	141.9	238.2	91.0	91.0	55.5	54.4	103.7
1281.0	17.8	1824.8	247.8	200.2	308.8	117.4	116.5	58.2	59.3	123.1

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1288.0   10.1  1272.1  226.2  146.5  249.2   90.7   78.7   48.4   57.7  105.6
1298.0   12.7  1103.0  228.9  146.4  232.5   87.5   81.1   45.2   62.8   99.8
1308.0   10.4  1392.5  217.9  182.1  306.0  106.7   68.0   40.7   73.8  109.4
1320.0   13.3  1708.2  226.0  196.0  315.7  110.5   76.4   41.1   61.8  117.1
1327.0   11.2  1134.8  191.0  118.8  196.7   77.8   59.4   36.3   59.5   86.0
1335.0    9.3  1066.7  202.5  147.9  240.7   89.1   71.3   40.9   55.3   88.3
1344.0    8.0  1299.1  238.1  164.0  266.4   96.6   65.9   39.9   62.6   99.3
1349.0    9.4  1139.9  252.4  146.3  242.8   88.0   66.9   38.0   57.0   96.0
1359.0    7.1   739.9  265.3   96.1  169.3   61.4   56.3   28.1   46.2   60.6
1369.0   11.0  1348.3  309.3  160.3  256.6   94.0   79.0   41.5   63.2   96.5
1379.0    8.6  1127.7  285.0  133.5  217.9   76.7   69.3   40.5   61.4  107.8
1389.0    9.8  1219.4  252.4  151.3  251.4   88.9   65.0   40.7   63.3  112.1
1398.0   11.3  1805.4  225.4  189.4  301.9  105.8   61.8   35.8   72.4  110.2
1410.0   15.2  1632.5  208.7  201.6  320.8  109.8   74.7   46.9   66.2  118.0
1420.0   16.4  1973.7  203.9  228.0  372.1  136.6   84.8   49.8   73.2  126.6
1430.0    8.3  1518.4  162.1  168.5  273.5  101.5   78.7   40.7   51.9  112.2
1438.5    4.0   817.3   70.5   92.6  158.3   61.6   12.3    9.1   13.0   86.9
1446.0    3.8   721.0   68.1   74.2  131.0   47.0    8.7    4.3   10.2   77.4
1453.0    4.9   694.0   52.1   80.0  135.8   51.2    6.4    5.6    8.2   78.3
1464.0   10.7  1211.9  216.6  135.0  228.9   83.1   68.3   45.4   57.5  110.0
1475.0   12.5  1651.6  238.8  189.1  301.7  106.6   77.8   50.9   71.4  117.3
1486.0   11.4  2245.1  259.6  232.4  388.6  130.7   74.7   48.2   88.2  142.5
1496.5   10.1  2152.8  274.9  243.4  405.9  141.2   73.3   44.2   92.1  149.9
1507.0    9.9  1855.2  272.5  199.7  335.2  117.6   70.4   42.9   85.9  139.6
1517.0   13.0  1874.0  294.8  215.8  337.9  117.5   74.8   44.5   87.9  125.8
1527.0   12.9  2489.5  288.8  274.9  424.2  149.5   80.5   48.7   85.4  142.4
1537.0   12.9  2247.5  280.6  259.5  409.9  144.5   76.9   48.5   89.8  143.8
1595.5    9.8  2436.7  208.0  183.6  285.9  111.1   46.8   29.1   70.1  131.0
1605.5    9.9  2751.7  247.1  213.9  326.6  124.4   54.3   33.6   73.5  123.1
1618.0   11.8  2429.0  239.4  205.0  293.7  109.6   64.3   38.0   58.5  138.1
1627.0   13.1  3141.5  282.3  339.8  502.5  178.8   77.6   40.6   87.1  144.2
1636.5    9.7  2020.6  235.5  207.4  308.8  118.7   63.0   41.0   69.5  128.1
1645.5   11.0  1794.1  158.9   77.3  118.0   64.6   52.0   23.8   29.7   78.6
1654.5    9.6  1248.1  205.2  157.6  236.0   95.6   48.5   37.6   56.6  122.9
1664.5   12.5  1384.5  235.0  180.4  283.4  106.6   68.2   41.8   60.6  113.8
1674.5   10.7  2216.9  166.9   65.8  106.3   64.9   60.0   17.8   27.3   79.3
1685.0    5.3  1202.3  192.2  140.2  211.3   84.3   39.0   35.8   60.5  117.0
1695.0   12.9  1605.9  233.7  211.4  349.7  134.2   72.9   43.6   70.8  116.6
1704.0    3.2   948.6  220.8  112.0  160.4   68.8   38.3   31.4   47.7   95.0
1727.0   11.6  2246.4  214.4  218.6  348.2  132.9   53.1   30.6   87.5  111.2
1746.0   11.1   820.3  215.7  106.4  147.6   57.5   49.0   65.5   39.8  104.3
1756.5    6.7  1636.4  279.0  196.0  297.2  110.7   54.6   45.8   67.4  118.8
1765.5    3.3   879.1  183.9   99.3  139.6   58.9   32.6   37.7   46.2   87.8
1774.5    2.5   988.9  176.4   99.6  162.2   62.2   22.4   22.2   56.2   70.2
1783.5   -0.3   363.6  139.8   33.2   25.2   20.7   12.9   22.2   22.0   46.3
1794.0   -0.1   614.2  136.1   59.7   86.2   40.1   17.2   27.5   32.4   61.6
1804.5   -1.6   356.1  149.0   32.4   23.8   23.9   20.6   29.8   23.8   56.9
1821.5    7.8  1630.0  222.9  182.5  266.0   98.9   60.9   49.0   62.0  114.8
1832.0   12.0  1700.8  238.5  200.2  308.3  116.4   64.4   59.3   64.6  146.4
1842.0    9.1  2306.0  261.8  268.1  412.9  146.9   79.4   55.9   72.5  151.2
1851.0   10.3  3010.2  239.7  270.2  395.7  143.5   61.2   50.5   74.7  147.9
1860.0   10.3  2146.0  203.5  194.6  288.1  107.1   63.9   46.4   62.8  115.5
1869.0   12.1  2168.3  195.1  186.6  277.2  107.3   62.5   43.8   63.7  115.2
1878.5   10.0  2851.3  226.1  241.4  386.9  146.1   76.4   42.0   84.2  127.3
1888.0    6.5  2502.4  227.0  220.1  337.4  132.4   64.2   35.2   83.5  119.0
1898.0   16.4  3041.5  240.6  263.6  411.1  150.4   75.1   40.6   91.3  135.3
1909.0    9.7  3215.1  235.4  287.9  444.8  162.4   74.6   32.4   98.5  134.0
1929.0   10.7  2757.8  212.4  220.6  355.9  131.1   65.7   33.0   86.4  120.5
1940.5    7.6  3320.8  249.5  279.6  444.3  159.1   86.7   37.6   97.1  140.0
1949.5   12.5  3472.6  228.0  290.6  457.6  169.3   80.9   34.5  100.1  140.2
1959.0   10.6  3383.8  222.9  255.4  404.7  148.8   82.7   33.1   91.0  133.2
1969.0   13.4  3598.6  248.0  299.3  471.3  168.8   95.2   40.4   98.5  150.9
1979.0   13.8  3484.4  238.9  281.3  445.4  153.7   85.0   32.8   98.2  132.5
1988.0    9.7  3293.4  249.1  276.0  426.7  156.8   97.7   39.4   92.1  137.4
1997.5   13.7  3513.0  245.5  291.9  462.7  161.1   90.7   38.1  101.4  151.0
2006.5   14.7  3757.0  250.1  293.0  463.9  166.6  106.0   39.5   97.4  147.0
```

```
2015.5   17.1  3775.1  254.9  291.3  455.7  161.1  110.0   48.9   89.8  155.8
2026.0   11.8  3811.4  252.4  298.8  450.4  165.6  114.2   45.3   91.4  145.6
2035.0    9.1  3659.8  261.5  298.2  460.3  167.8  114.5   44.1   88.6  169.5
2044.0   14.6  3828.9  258.2  294.0  469.2  170.3  119.0   48.1   88.9  151.4
2053.5   14.2  3772.6  251.7  290.9  449.5  166.7  117.1   47.3   83.1  155.6
2064.0   14.3  3995.3  271.6  316.8  474.0  166.9  119.1   46.9   88.8  164.5
2080.0   15.2  3864.8  272.4  308.4  459.2  164.0  121.2   48.0   85.1  148.6
2096.0   12.3  3811.7  250.7  303.3  445.7  161.6  125.1   53.2   80.1  159.5
2114.0    8.8  4104.3  238.7  310.9  470.2  164.3  110.2   38.7   93.7  152.2
2239.5   15.4  2606.3  236.2  209.0  320.9  128.8  157.9   54.0   56.6  123.0
2248.5    6.6  1763.8  242.5  176.0  269.2  102.8   50.9   39.5   67.5   96.9
2258.0    6.8   536.2  184.9   84.3  139.0   56.3   31.2   29.9   34.0   65.7
2267.0    7.1   697.9  166.7   96.4  160.6   66.3   36.6   28.7   31.8   74.3
2276.0    6.2   964.6  201.8  136.6  208.8   82.7   48.6   40.0   46.9   82.2
2285.5    1.0   443.8  184.3   62.6   88.9   37.5   26.7   40.0   43.6   59.7
2294.5    2.6   521.6  172.3   69.7   87.0   41.2   28.4   40.2   47.7   66.5
2303.5    6.0  1068.4  138.8  109.2  153.3   55.1   29.8   27.1   40.7   77.0
2313.0    9.2  1060.7  189.8  127.5  208.4   79.5   49.5   45.8   49.9   82.3
2349.5   14.2  2105.3  217.5  207.9  340.5  134.5   92.2   53.1   68.4  116.4
2360.0   15.5  1930.0  221.1  223.4  337.5  127.4   77.2   45.0   73.9  119.7
2370.0   14.5  1070.6  209.7  153.3  259.5  104.4  107.2   59.9   46.4   99.8
2379.0   11.0  1461.0  218.7  190.2  296.7  115.2   82.8   51.4   65.6  114.3
2389.0   12.8  1955.1  236.0  217.8  345.8  136.5   68.2   41.9   81.9  123.0
2399.0    7.8  2334.0  217.1  218.7  349.5  134.9   62.2   42.2   79.2  121.2
2413.5    9.6  2482.9  216.4  235.3  378.9  143.4   65.1   38.9   83.6  127.4
2423.0   15.8  2020.4  223.2  243.4  381.6  146.7   73.7   41.1   78.0  128.0
2432.5   14.5  2156.0  225.0  294.1  433.7  155.9   78.1   44.6   77.3  135.0
2445.5   10.6  1428.9  160.5  212.6  340.8  128.1   81.2   39.3   47.0  127.9
2457.5   11.3  1188.1   97.3  157.3  262.3  103.8   37.2   18.9   27.0  126.1
2470.0    8.1   962.3   53.6  116.3  191.7   78.4   15.2    5.2    8.3  110.4
2480.0    7.0  1487.2  162.7  203.2  341.1  125.9   46.3   25.6   53.1  128.3
2490.0    9.4  1305.0  171.5  208.9  336.8  120.1   54.9   33.1   52.4  127.4
2499.5   11.0  1396.9  188.2  170.0  280.7  107.1   61.0   41.2   56.3  110.3
2508.5    5.4  1188.7  175.9  136.3  228.4   89.4   44.0   31.0   52.6   95.2
2518.0    5.4  1191.1  219.0  155.7  254.8   99.2   67.6   47.0   59.4   96.1
2527.0   11.2  1406.7  220.1  174.1  284.0  112.3   67.4   49.4   60.7  101.8
2549.5    9.4  1129.8  200.8  146.0  225.2   86.4   73.8   52.7   52.0   97.2
2561.0    7.3  1881.2  181.4  144.7  233.8   92.7   43.1   29.3   57.6   87.9
2570.0    9.2  1173.0  269.7  115.2  177.6   72.1   52.6   52.6   70.9   74.3
2579.0   11.7  2538.4  239.3  187.6  312.3  123.5   56.6   48.3   76.5   98.5
2588.0    9.6  2418.2  235.1  197.4  327.7  121.3   80.3   54.5   74.7  107.0
2609.5    9.3  3330.2  227.5  260.7  432.8  160.8   60.1   38.5  100.2  120.3
2620.0   10.2  1712.8  218.1  223.2  346.9  128.8   66.2   49.6   76.4  122.5
2631.5   11.0  1797.5  188.8  223.4  356.5  132.1   57.9   40.4   64.5  126.9
2645.0   12.2  1202.7  242.2  164.1  262.7   97.6   85.7   63.9   59.0   96.4
2654.0   12.4  2106.8  216.3  196.0  316.5  119.3   58.0   44.8   65.5  102.5
2663.5   13.1   967.9  196.8  131.6  211.5   83.1   62.8   55.7   39.1   88.5
2672.5    1.7  1213.3  292.3  119.1  160.7   67.9   50.7   56.8   60.0   74.3
2681.5    8.3   975.9  280.3  138.4  203.8   83.4   76.3   70.3   43.7   81.2
2690.5    9.2  1097.6  326.7  145.3  226.2   89.0   77.7   71.1   49.6   81.3
2699.5    5.3   886.4  371.2  102.8  159.1   72.7   64.5   69.1   43.4   68.7
2708.0   10.1   945.6  371.3  111.1  171.5   72.4   94.1   81.1   44.9   75.2
2717.5    5.2   829.5  422.2  100.0  163.0   65.2   65.8   61.0   45.1   66.3
2729.0    7.3   953.4  469.2  123.5  194.0   75.2   60.6   28.2   45.8   57.0
2748.0    8.3   890.3  445.7  116.0  170.1   69.3   64.0   34.3   43.3   85.2
2826.5    5.9  1137.3  383.1  141.7  217.2   90.1   83.0   45.4   53.8   79.3
2855.5    6.0   914.6  316.9  136.4  210.3   80.2   42.0   23.1   38.5   97.3
2874.0    7.2   776.4  283.7   96.2  153.7   64.0   72.2   36.5   35.2  114.0
2883.0    0.4   577.9  381.7   74.7   89.3   44.0   54.3   36.1   55.8   97.0
2892.5    7.4   785.5  275.7  106.1  170.0   67.4   59.8   52.0   43.7   89.1
2902.0    8.4   874.0  254.7  135.0  212.4   79.6   61.1   43.8   41.8   82.1
2911.0    9.1   829.1  237.7  126.1  209.5   86.8   62.4   42.9   43.3   94.4
2920.5    8.7  1626.4  261.3  194.2  321.6  115.4   66.0   38.3   71.7  101.0
2930.5   11.0  1103.9  243.3  158.3  253.4   97.8   87.7   60.3   54.3  104.3
2952.5   12.2  2081.7  236.8  217.6  361.6  119.2   63.9   38.7   78.9  105.9
2964.0    9.0  1038.0  230.0  139.0  220.3   79.9   73.4   48.0   48.2   86.6
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2976.5    7.4   750.8  215.8   98.4  156.0   60.3   56.3   47.0   36.1   84.7
2989.5   11.6   798.3  247.8  101.3  158.5   61.8   52.1   47.5   43.9  101.2
3000.0    5.6   714.0  267.3   94.0  161.6   59.6   66.6   52.1   39.8  104.9
3011.5    7.1   638.5  228.1   69.9  122.0   43.7   39.2   44.2   37.6   70.0
3021.5    1.9   399.6  214.5   57.0   84.2   33.6   46.0   45.5   28.1   64.7
3031.5    4.7   331.1  202.2   42.7   59.9   23.3   33.7   46.3   23.7   68.2
3044.5    4.3   259.1  162.9   28.3   45.3   15.0   23.5   43.8   19.9   57.2
3056.0   -2.7   425.6  192.1   52.0   65.3   26.3   32.7   40.2   36.0   54.7
3067.5    0.8   359.4  267.6   39.8   63.2   26.0   36.6   33.3   37.7   64.4
3078.0    6.7   641.7  206.3   83.9  140.0   49.4   41.6   42.2   38.2   87.0
3088.0    5.9   896.5  229.8  118.4  192.5   67.1   59.7   48.4   53.0   86.1
3098.5    7.1  1299.2  241.1  153.3  251.6   91.5   79.3   47.1   62.4   86.1
3110.0   13.6  1280.4  235.5  158.7  269.0   95.7   92.2   55.4   55.8   92.6
3122.0   12.7  1223.4  269.9  178.9  296.6  108.9  112.5   65.0   58.8   99.9
3155.5    9.3  1032.9  260.0  152.1  247.5   96.1  102.9   60.8   48.0   90.9
3166.0    6.9   817.2  215.0  131.5  224.3   74.7   54.4   40.8   41.5   92.7
3176.5    9.9   871.5  268.8  131.5  211.0   79.9   67.1   56.4   47.8   79.5
3187.0    7.2   711.8  304.7   99.5  173.5   63.1   64.9   51.5   41.3   79.6
3197.0    4.9   612.9  388.7   83.5  119.5   43.4   57.1   39.6   44.1   68.1
3207.0    5.5   695.1  290.8   99.8  154.4   57.9   54.1   44.6   38.1   72.0
3217.5    7.1  1095.5  359.0  147.6  251.7   81.9   81.3   53.7   51.2   79.2
3226.5    9.4  1153.8  349.6  147.2  263.7   87.5   69.6   46.9   58.8   79.9
3236.5    7.9   987.0  323.9  114.3  189.8   64.7   59.3   39.0   43.5   69.0
3249.5    7.1   647.9  361.7   93.8  161.0   55.5   63.1   55.8   41.0   85.4
3258.5    7.9   827.3  409.1  113.8  191.5   71.5   78.7   44.5   42.1   92.2
3268.0    7.7   703.7  365.6   95.7  174.6   60.7   56.1   37.1   42.1   83.3
3277.0    9.3   746.9  383.5  109.9  180.6   72.0   69.9   35.8   35.5   91.5
3286.5    7.3   699.4  353.6   87.0  159.2   64.4  102.0   39.4   25.5  108.9
3297.5    7.3  1003.4  349.9  111.1  188.0   65.7   36.0   18.3   38.3  103.5
3307.5    8.0   563.2  417.5   73.2  132.2   46.0   40.8   30.1   39.2  137.0
3317.0    4.3   256.3  388.8   37.4   63.5   24.9   34.3   37.0   23.7  146.7
3326.0    4.3   445.2  401.4   65.0  120.1   35.5   58.9   35.2   23.2  108.6
3337.0    3.5   397.2  407.5   50.3   95.3   34.5   47.8   42.5   25.1  143.4
3356.5    1.5   263.5  422.0   38.4   56.7   26.6   36.4   24.4   23.6  101.6
3367.0    2.9   306.4  458.9   49.5   74.7   24.5   46.2   35.6   24.0  167.0
3378.5    1.2   985.5  468.2   89.1  147.5   53.2   47.7   30.4   41.9  187.2
3390.0    2.6   304.6  475.5   38.3   58.6   22.9   36.8   25.3   21.2  142.8
3402.5    0.5   237.7  464.1   32.6   55.5   19.8   34.0   18.3   22.2   47.1
3412.0    3.0   341.9  492.3   49.6   82.9   31.5   52.4   27.3   22.5   53.9
3422.5    3.1   512.6  424.7   69.9  110.3   39.7   41.8   23.4   26.3   68.0
3433.5    4.8   634.8  393.4   80.5  130.4   50.4   52.3   26.4   33.3   63.9
3444.0    7.8   723.3  370.2  126.7  201.8   66.6   40.5   24.5   39.7  102.7
3454.0    7.3  1345.6  391.3  199.6  332.1  116.1   69.1   32.6   62.5   93.1
3464.0    5.0  1314.2  370.9  159.5  255.4   92.3   47.7   28.5   65.1  105.3
3474.5    7.7  1117.7  354.0  159.5  264.8   95.5   67.4   37.0   54.7  110.4
3485.0    8.4  1417.5  333.5  174.9  293.8  100.8   56.4   29.5   71.9  135.8
3495.5    9.1  1005.6  333.8  142.5  241.1   87.7   79.7   37.8   49.5   71.4
3504.5    8.0  1258.0  323.4  147.7  250.7   89.7   84.5   47.5   53.0   78.2
3514.5   10.5  1412.2  301.2  152.6  245.7   92.3   69.0   38.3   58.1   79.0
3524.5    4.2  1538.9  253.7  166.5  276.3   94.9   52.8   27.6   54.6   85.7
3534.0    6.1  1988.7  318.4  192.5  324.6  112.7   63.2   34.3   81.6   91.4
3543.0    8.7  1377.8  314.5  165.9  289.3   98.0   83.3   39.0   60.4   84.2
3561.0    4.1  1211.6  362.2  142.9  251.0   87.8   70.1   40.4   57.5   74.2
3571.5    2.5  1297.4  343.6  140.9  249.8   84.1   51.0   25.6   57.1   67.3
3581.5    7.4   879.8  349.8  118.0  194.4   68.0   49.6   26.4   45.1   52.0
3591.0    9.7  2206.5  322.8  198.5  332.7  116.0   44.5   23.2   83.3   79.6
3600.0    9.6  1889.2  272.7  170.8  298.6  110.4   63.0   30.4   62.0   93.9
3609.0    7.5  1424.8  322.0  174.6  285.5  103.2   85.1   44.1   60.2   91.5
3619.5   10.4  1537.2  328.2  188.1  305.1  107.1   80.0   41.1   72.1   91.6
3630.0    9.5  1452.6  312.8  181.4  299.4  103.7   73.3   39.2   66.5   90.2
3642.0    9.5  1005.0  318.7  156.6  255.6   87.2   83.8   43.1   53.3   87.9
3666.0    6.1  2054.7  319.1  234.4  369.8  126.0   54.0   28.8   85.3   91.3
3677.5   11.5  1528.7  344.9  228.6  373.6  127.4   58.8   28.6   83.4   89.9
3705.5    9.7  1247.1  250.5  201.0  321.2  107.4   49.9   28.4   62.5   84.1
3717.0    5.6  1352.9  296.2  201.3  323.5  105.3   64.0   35.2   63.8   89.3
3727.5   13.7  1623.0  316.9  218.1  351.9  130.4   72.3   38.4   69.5   99.4
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3738.0    6.7  1260.7  282.9  201.0  315.3  104.4   54.6   37.6   68.7   87.7
3768.0    5.8  1402.0  237.6  219.7  349.2  123.9   49.6   26.7   73.5  105.5
3779.5    7.0  1445.1  249.7  210.8  347.2  121.1   57.6   26.4   59.9  105.3
3790.0    7.1  1355.4  260.7  207.5  344.1  117.1   44.0   26.7   63.9  100.6
3800.0    9.3  1612.1  290.1  215.1  344.6  119.5   48.2   32.7   72.2  107.5
3810.5   10.0  1633.4  294.2  217.9  343.4  116.2   52.3   35.3   68.5  104.5
3854.0    7.7  1607.2  260.3  187.6  304.2  106.6   49.4   28.7   72.7   83.3
3864.0    8.4  2350.6  254.8  249.8  402.3  147.3   57.1   29.0   89.3  115.2
3876.0   11.1  2157.8  288.5  261.0  411.0  146.2   77.7   36.2   90.1  116.1
3886.0    6.0  2216.5  288.3  241.4  382.1  133.4   66.8   31.6   86.1  103.6
3896.5    7.6  2780.9  268.5  263.2  428.0  151.4   58.0   26.2  100.6  114.7
3908.5    8.6  2465.8  286.1  261.3  427.1  143.3   73.4   38.0   94.4  118.8
3919.5    8.2  2598.9  276.8  268.5  424.0  151.5   71.4   38.3   96.6  120.5
3938.5    8.4  1939.4  264.4  247.1  393.7  139.7   58.6   27.8   83.9  119.2
3948.0    9.5  2452.7  303.4  278.7  451.1  158.3   63.0   33.8   94.3  115.5
3957.0   12.2  2337.0  305.7  304.5  485.8  170.4   76.5   37.5   99.4  124.8
3967.0   13.5  2257.1  288.0  284.1  459.7  154.2   65.7   34.7   95.9  119.8
3977.5   11.8  2216.8  277.9  305.8  476.5  164.5   67.8   36.5  100.6  122.6
3988.0    8.4  2593.9  303.6  314.6  489.1  172.6   67.0   32.5  106.7  126.3
3998.0    9.8  2481.3  289.9  313.4  476.1  164.8   68.1   31.5  105.7  125.4
4008.5   11.3  2650.1  268.3  332.4  507.9  177.8   66.7   33.1  105.2  133.7
4017.5    9.9  2335.3  272.3  313.2  493.1  172.3   61.1   33.9  104.6  129.1
4029.0   13.6  2563.1  268.0  299.7  467.7  166.3   64.0   32.3  101.9  130.6
4052.0   14.3  2445.4  274.0  265.4  438.6  151.9   65.1   35.4   94.6  123.0
4062.5   10.2  2149.9  308.4  218.8  359.2  125.3   63.5   33.6   86.6  107.9
4073.0   10.5  2013.8  245.7  206.4  348.0  121.9   66.2   37.2   75.6  109.1
4083.5    8.7  2136.0  233.6  234.8  387.9  134.3   61.1   35.2   78.2  112.6
4097.0    7.7  2624.1  269.4  267.3  430.0  148.8   63.5   32.1   97.4  116.1
4106.5    6.0  2281.3  262.7  238.5  375.8  134.1   62.5   37.8   85.5  106.6
4120.0    9.7  1715.3  227.6  212.9  343.0  127.1   78.0   42.6   66.3  107.7
4130.5   13.4  1757.3  220.8  207.7  343.1  122.5   64.7   35.3   70.8  103.6
4139.5    7.7  1980.7  236.3  217.5  343.7  120.6   80.4   44.8   81.5  104.4
4149.0   11.1  1595.2  279.0  213.0  336.2  118.6   92.9   52.4   79.0  103.7
4158.0    9.9  2360.2  244.4  252.4  391.0  135.0   77.3   42.0   89.9  116.5
4167.5   14.2  2275.1  239.9  249.1  388.6  137.6   76.9   43.1   88.3  115.4
4176.5    9.7  2116.8  245.0  262.8  423.1  149.3   85.6   43.1   91.0  121.8
4185.5    9.4  2125.9  274.9  239.3  383.0  136.8   75.6   37.9   94.7  111.3
4210.0   16.5  2200.9  250.8  252.8  393.9  144.7   82.5   45.8   85.5  120.3
4220.5    8.2  2414.3  224.2  229.7  384.5  137.6   68.3   35.6   82.4  114.7
4231.0   10.1  1136.9  295.4  151.7  237.4   89.0   80.0   44.0   73.0   86.5
4241.0   13.5  1707.3  240.4  204.4  334.8  119.2   80.1   46.7   72.4  109.7
4251.5   19.3  1738.6  255.2  228.5  371.1  135.7  140.6   75.8   66.0  117.2
4262.0   11.5  1749.1  249.6  221.8  363.5  126.8   73.7   45.9   76.6  118.3
4272.5   12.2  1182.8  234.3  165.7  277.8   99.2   73.5   48.1   65.3  103.9
4281.5   14.3  2028.9  274.8  237.8  381.4  135.4   85.9   48.4   80.1  128.9
4290.5   13.5  1698.5  259.6  217.7  357.2  128.2   89.2   58.2   74.8  116.6
4303.5   17.6  1728.6  265.3  223.7  364.9  135.8   96.2   48.4   66.9  120.4
4312.5   16.6  1485.5  263.4  207.9  348.7  132.1  132.7   63.1   63.7  112.5
4323.0   13.6  2057.8  275.0  262.0  427.2  152.0   96.1   46.0   83.2  129.6
4333.0   13.8  2378.1  254.9  235.2  390.5  133.9   90.1   47.0   81.5  119.6
4342.0    9.7  1671.0  240.1  197.2  331.3  120.0   95.2   48.2   65.1  111.5
4351.0    9.2  1501.4  301.7  168.9  257.7  100.4   97.8   52.3   63.1   93.8
4361.0   10.1  1667.2  223.7  204.0  325.0  113.0   73.3   37.8   66.3  111.3
4371.0   16.2  1783.4  268.9  209.0  340.7  117.6   89.1   49.0   75.9  110.2
4380.0   10.8  1159.7  295.9  163.7  262.2   92.0  100.6   64.3   56.3  107.2
4390.0   11.1  1322.0  297.3  153.9  255.6   92.5   92.4   66.7   58.8  116.1
4412.0    9.2  2423.5  293.6  237.4  381.2  142.1   83.0   53.9   83.0  124.9
4421.0    8.2  1513.3  279.1  198.8  316.2  123.9   97.0   65.2   60.8  111.0
4437.5   10.3  2335.6  277.2  238.2  390.8  148.6   78.7   47.6   81.3  115.2
4446.5   13.5  1990.2  279.3  225.9  356.2  135.7   96.2   65.0   73.6  109.3
4456.0   12.6  2015.2  241.6  194.2  304.8  121.6   84.2   51.2   61.7  102.6
4465.0   12.4  1279.3  296.2  183.8  284.7  107.2  102.3   68.8   63.7  101.0
4473.5   16.4  1272.4  268.3  175.1  277.0  110.8   85.9   64.5   66.9  109.1
4486.0   18.9  1658.1  266.7  189.9  315.7  127.0  159.9   82.6   61.8  108.0
4496.0   14.8  1444.2  283.7  201.1  296.7  119.3  121.8   76.6   62.3  106.7
4509.5   13.6  1565.4  257.7  184.2  310.3  120.1   98.2   72.0   67.6  108.2
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4519.0   13.8  1463.5  261.9  194.3  320.7  127.3  121.1   80.7   59.5  111.6
4528.0   16.4  1483.0  272.2  191.3  298.6  119.6  119.0   83.4   62.6  103.9
4548.0   14.4  1742.9  255.4  190.1  314.9  127.3  183.0  117.7   55.8  179.7
4556.0   16.9  1966.0  276.5  204.6  344.4  138.5  131.5   97.8   69.6  117.3
4564.0   14.2  1766.9  255.5  196.9  325.3  125.5  100.9   72.5   71.9  111.2
4577.0   18.2  1659.4  261.6  226.6  360.6  144.3  132.2   67.2   67.0  122.7
4588.0   13.6  1954.4  245.8  184.4  290.6  112.6   95.9   57.4   66.5  109.7
4597.5   14.3  1947.8  268.0  201.4  317.5  124.7  111.0   65.7   71.8  115.0
4607.0   16.9  1929.2  268.5  269.8  422.0  152.3  101.5   54.3   82.5  127.0
4618.0   14.4  1597.0  247.2  217.8  351.5  121.1   88.9   50.8   69.5  113.8
4630.5   14.2  1178.7  274.7  163.8  260.0   98.2  118.2   67.5   56.8  104.9
4641.0    9.7  1446.9  269.7  178.4  295.7  108.5  100.5   54.9   64.4  102.1
4651.0   12.1  1199.4  275.2  163.6  264.1   99.3   92.5   57.1   58.9  101.0
4661.0   13.3  1212.0  286.7  156.3  265.1  100.2  189.6   84.8   48.9   94.4
4671.5   12.7   868.1  260.6  128.8  212.2   79.9   91.4   57.6   50.0   92.4
4681.5    9.4  1456.0  274.4  192.0  309.5  107.8   94.5   59.5   69.2   99.4
4691.5   20.6  1464.6  320.3  227.0  366.5  141.1  256.6  122.0   51.7  113.5
4710.0   15.1  1807.9  297.0  198.9  316.0  114.5  109.6   56.5   61.7  108.7
4718.5    7.2  1589.4  248.7  160.3  260.0   90.8   81.9   58.6   60.5   98.7
4730.0   11.8  1995.9  250.6  168.1  283.7  101.7   77.9   51.3   63.4  101.6
4740.0   10.6  2337.0  262.6  189.1  318.2  112.7   68.6   46.9   69.8  100.9
4751.5    3.9  1061.2  200.0  149.9  246.5   86.6   55.7   40.1   42.1  102.2
4763.0    7.9   875.4  176.5  144.9  246.3   89.9   59.5   43.5   38.0  104.0
4773.0   15.0  1319.8  285.3  201.9  333.2  124.9  137.8   78.2   60.8  112.5
4822.5   16.6  1951.8  285.2  244.9  383.2  144.1   84.2   42.7   88.0  120.6
4839.0   15.8  2307.8  259.0  224.9  366.9  140.4  137.1   71.2   78.6  113.7
4849.5   11.1  2100.1  255.0  237.3  366.7  138.4   69.9   44.5   82.9  114.6
4859.5    8.4  2066.9  279.8  192.7  318.2  105.2   63.7   43.7   72.7  107.7
4870.0    7.7   867.9  259.6  129.2  212.9   78.2   68.0   54.1   45.6   97.9
4880.0    9.6  1174.6  271.6  144.0  251.3   86.9   46.5   37.7   65.8   93.7
4893.0    7.8   831.9  262.7  108.7  190.4   69.3   78.0   41.9   43.3  106.5
4902.5    6.9   635.8  321.3   80.8  144.6   55.2   67.0   54.5   31.3   87.8
4913.0    6.5   678.1  247.7   95.6  159.7   60.5   55.0   47.6   43.4  103.3
4923.5    3.8   365.4  191.8   49.9   84.0   32.5   30.6   44.2   29.1  111.2
4933.0    0.8   649.5  237.4   82.8  136.1   51.8   43.8   48.2   48.0   84.1
4943.0    6.9  1052.9  247.4  128.9  225.0   81.5   49.0   49.5   59.2   95.6
4953.5    4.5  1081.5  219.0  150.0  233.0   85.0   46.4   44.2   59.6   89.2
4962.5    7.8  1154.6  271.5  164.8  259.2   93.7   70.7   52.3   72.7   91.2
4971.5   16.7  1433.3  242.2  210.6  337.7  118.0   89.8   58.9   64.3  110.1
5006.5   13.1  1688.0  224.8  176.5  293.0  114.3   91.6   60.8   64.7  100.3
5015.5   12.4  1455.1  255.7  189.6  297.2  116.7  146.9   80.9   60.2  104.6
5025.0   13.1  2565.5  227.0  209.6  349.8  128.9   74.8   44.3   84.2  108.6
5034.0   11.3  2690.6  230.7  210.3  350.4  136.7   81.1   50.8   84.3  108.6
5043.0   15.8  2229.9  248.6  254.1  397.3  145.5   92.4   61.0   85.9  120.4
5052.0   14.1  2255.9  239.4  284.8  447.7  165.4   85.8   54.8   89.8  130.0
5061.0    7.4  2065.1  184.3  265.5  412.8  156.1   53.5   32.2   78.4  125.7
5070.0    9.2  2417.5  228.9  319.4  502.4  182.6   67.2   35.9  101.0  126.4
5079.0   13.8  2215.6  219.0  271.1  442.3  159.5   68.0   38.7   87.5  121.2
5089.0    9.5  2116.3  250.9  229.7  361.0  137.3   80.8   56.1   84.6  107.4
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depth	Pb	Th	U	Rb	Sr	Y	Zr	Nb	Cl	S(wt%)
5.0	26.7	14.1	6.1	174.7	647.7	16.9	154.1	20.0	1450.4	1.51
15.0	16.7	5.5	-1.1	28.4	181.0	4.2	42.5	7.6	596.0	4.00
25.0	10.4	4.5	1.1	26.4	422.8	3.9	43.7	8.3	399.6	3.27
35.0	9.1	6.1	1.1	25.5	383.4	4.5	44.3	8.5	311.6	2.90
45.0	8.3	4.7	0.1	21.0	164.3	3.6	33.8	7.0	422.7	3.94
55.0	4.7	4.1	1.2	19.5	89.5	2.7	24.9	4.9	294.9	2.63
65.0	7.4	4.9	3.2	19.4	80.4	2.1	21.8	4.6	275.0	2.89
75:0	7.9	4.7	1.0	31.8	90.7	3.5	36.1	5.9	422.4	3.86
85.0	8.2	4.1	-1.9	21.1	80.6	4.3	28.1	6.1	361.0	4.39
95.0	4.7	2.7	0.6	13.5	111.1	3.4	16.9	5.4	438.1	5.83
105.0	24.6	12.6	3.8	128.7	467.5	10.4	111.6	20.2	1325.6	1.58
115.0	42.7	23.6	10.6	257.2	992.4	19.9	216.9	40.9	2817.6	0.89
125.0	12.9	5.4	-0.4	40.2	165.5	4.3	45.8	9.3	663.5	2.71
135.0	13.0	3.1	1.0	12.3	62.3	2.5	20.7	4.8	444.4	2.64
145.0	10.5	3.4	-0.8	12.3	56.9	2.5	20.5	4.6	359.8	2.53
155.0	14.6	4.2	-0.9	13.8	55.6	2.5	21.3	4.4	386.9	2.50
165.0	21.3	3.8	0.7	16.4	63.5	2.7	24.7	5.3	291.6	2.55
183.0	9.0	1.9	4.1	14.8	67.0	3.2	22.1	3.9	306.3	3.10
193.0	7.8	1.5	3.2	14.8	68.0	3.5	23.5	3.7	291.1	3.04
203.0	9.6	1.1	2.4	13.3	64.4	3.3	19.7	3.8	298.5	2.97
213.0	7.0	0.5	2.1	11.7	52.5	2.9	16.7	2.9	342.0	2.91
223.0	7.7	2.7	2.6	24.5	87.9	4.8	37.5	5.7	493.7	3.64
233.0	10.0	4.9	3.4	32.0	100.0	6.9	53.5	8.5	522.8	3.80
243.0	13.1	8.1	3.0	54.9	80.3	9.0	84.8	12.8	1114.1	3.61
253.0	7.5	2.8	2.3	22.4	77.1	4.9	33.1	5.0	769.7	4.03
263.0	6.5	2.4	5.7	19.2	70.6	4.4	27.7	4.5	594.3	3.52
273.0	4.9	0.9	7.0	14.9	65.4	3.7	20.3	2.7	512.7	4.01
283.0	4.0	1.4	5.6	14.4	58.2	3.7	19.1	3.2	530.6	3.54
293.0	4.4	0.3	3.4	13.5	55.8	3.2	17.5	3.5	545.5	2.12
303.0	7.8	2.6	3.5	26.6	90.8	4.0	31.7	7.4	487.0	2.34
310.5	25.8	14.1	7.6	142.6	412.1	12.9	131.4	20.2	1117.9	2.91
315.5	50.8	32.6	9.2	322.8	854.3	22.5	275.6	42.1	2051.9	0.35
320.5	55.1	34.9	11.3	310.9	799.3	22.5	287.5	44.0	2576.0	0.43
327.5	13.1	6.8	4.2	59.6	166.6	8.1	62.6	12.7	675.4	1.23
335.5	54.0	33.8	8.6	317.5	743.5	20.7	291.4	45.9	1427.5	0.29
343.0	5.2	2.6	4.4	23.5	88.2	5.2	33.2	9.3	802.7	2.64
353.0	20.5	11.8	5.7	90.0	183.4	6.1	104.2	16.2	827.2	2.33
362.5	9.0	3.8	6.6	32.8	97.4	7.0	52.0	6.7	716.1	4.00
377.0	30.6	17.7	7.1	146.1	330.7	14.6	166.0	23.7	1762.3	2.06
387.0	14.6	4.5	7.7	37.0	106.1	6.3	56.8	8.4	777.4	2.89
397.0	9.4	2.0	7.2	19.5	87.6	3.5	25.7	4.2	481.9	3.38
407.0	8.6	1.5	7.8	18.2	92.9	4.4	31.3	5.0	424.7	4.55
417.0	10.3	1.6	11.0	16.6	82.4	3.6	28.2	4.7	470.5	6.10
427.0	16.9	6.0	9.4	51.2	162.6	7.2	70.2	9.5	850.7	3.89
437.0	10.4	0.9	6.1	15.9	62.6	3.0	22.8	3.6	487.3	3.03
447.0	24.8	13.2	5.6	109.8	206.5	12.3	141.1	18.5	1692.5	1.50
457.0	9.7	0.4	9.7	11.5	71.9	3.6	19.0	4.0	487.1	5.27
467.0	8.4	0.1	9.6	10.4	61.0	1.9	13.6	3.0	579.3	4.19
477.0	10.0	3.2	8.1	28.7	99.8	3.8	40.2	6.5	649.7	7.49
487.0	6.0	0.9	10.3	10.5	57.5	2.2	15.0	3.1	405.9	4.82
497.0	7.4	1.2	10.2	13.4	61.1	3.3	21.9	3.8	426.7	5.22
507.0	20.8	18.4	13.6	123.6	86.2	18.2	209.0	28.8	1411.4	3.70
517.0	7.2	-1.7	10.4	6.9	64.2	2.1	11.8	2.7	404.2	4.94
527.0	6.2	-0.8	7.3	5.5	43.5	1.2	7.9	1.9	282.7	3.78
537.0	6.2	-0.7	4.1	3.3	32.1	1.0	4.3	0.6	240.3	2.36
547.0	6.2	-1.0	5.7	5.3	37.2	1.5	6.4	1.9	314.3	2.54
555.0	6.2	0.3	8.5	6.5	42.9	1.2	8.1	2.4	360.2	2.87
562.0	5.3	-0.4	11.8	6.4	46.3	1.8	8.0	2.6	352.8	4.07
577.0	4.6	1.2	8.2	22.5	80.7	2.8	28.5	4.9	426.3	3.89
587.0	4.2	0.3	9.3	13.5	66.8	2.3	18.9	4.0	475.5	4.41
597.0	4.6	1.1	10.7	17.6	73.9	4.1	25.0	6.3	436.2	5.45
607.0	5.4	2.6	13.5	20.4	109.9	6.7	36.1	7.2	372.9	5.34
617.0	9.9	6.2	15.4	35.6	160.3	7.1	58.1	10.3	386.1	3.76
626.0	41.1	26.2	13.4	217.7	494.1	19.3	244.2	34.9	1218.7	1.25
634.0	18.1	10.8	13.5	76.5	263.1	10.4	120.0	17.0	830.3	2.97
642.0	45.7	31.5	17.0	197.2	402.8	14.0	280.6	34.7	1818.6	1.82
649.5	90.0	64.8	24.2	417.5	368.2	17.7	592.9	70.2	3897.0	0.48
657.5	62.4	46.6	19.2	284.4	290.2	13.9	414.9	50.4	2708.9	1.60
667.0	16.5	9.0	8.9	71.8	171.8	9.8	94.5	13.9	1232.3	4.92
677.0	34.2	20.0	9.9	150.8	280.3	17.4	179.6	22.7	2317.6	2.91
687.0	6.3	-1.0	10.1	7.1	62.9	2.4	9.5	3.2	534.3	5.42
697.0	5.9	-1.5	11.0	6.8	59.3	2.9	10.1	3.6	431.0	5.51
707.0	7.8	0.7	9.9	8.6	63.3	3.7	13.0	3.1	447.0	4.09
717.0	8.1	1.0	6.6	9.1	71.3	3.7	15.5	4.0	337.4	4.09
727.0	7.7	0.5	4.9	10.2	70.7	3.5	17.5	4.5	333.0	3.66
737.0	8.1	0.3	5.1	14.6	71.4	3.8	25.7	6.9	255.3	2.86
747.0	19.4	10.3	6.9	76.0	257.2	13.6	116.8	15.7	818.0	1.79
756.5	24.4	14.1	5.9	74.1	343.0	16.5	129.1	21.2	663.2	1.89
776.5	28.0	18.1	5.6	127.3	444.1	19.7	166.3	22.5	1468.5	1.09
785.0	43.2	24.7	8.7	261.4	787.9	27.5	261.2	35.6	3650.3	0.52
794.0	15.4	9.4	4.9	64.1	224.3	12.0	96.9	16.7	669.4	1.95
804.0	17.7	9.9	6.4	56.5	212.8	15.2	106.2	16.4	376.8	2.62
814.5	16.9	10.5	5.6	66.1	281.6	18.0	105.4	15.1	636.7	3.26
825.0	7.7	3.7	7.2	28.9	145.0	11.6	53.3	13.4	395.1	5.51
835.0	10.5	4.5	8.1	26.0	117.5	10.5	54.9	12.2	272.5	4.05
845.0	15.3	10.6	6.7	56.7	110.8	13.8	112.4	17.3	545.3	1.70
855.0	19.2	11.1	5.5	55.0	190.7	15.1	105.0	15.9	478.4	1.03
865.0	35.7	23.3	6.0	201.8	362.1	24.4	235.6	32.6	2232.1	0.91
877.0	32.8	22.6	7.8	152.8	207.8	21.5	208.8	29.4	1183.2	0.63
887.0	33.2	25.1	8.2	154.4	222.7	25.6	239.3	34.8	1678.3	1.04
897.0	28.2	18.5	6.4	113.7	265.0	23.2	188.1	28.1	876.4	0.70
906.0	39.7	26.1	7.7	190.1	321.2	25.1	249.8	34.8	1519.2	0.49
915.0	32.4	23.1	5.7	95.7	307.6	27.2	208.5	35.1	424.6	1.25
924.5	39.1	27.0	7.4	119.2	332.7	31.2	236.4	39.2	406.1	0.90
932.5	52.3	57.6	15.3	312.5	135.5	46.1	611.5	73.3	2260.8	1.02
941.0	31.0	22.1	7.5	76.7	297.1	26.6	192.3	32.7	189.3	1.56
951.0	41.4	36.3	10.7	127.0	338.6	33.6	295.3	46.8	644.4	0.92
961.0	37.9	29.9	8.7	94.7	341.1	30.8	240.8	39.8	323.9	0.61
977.0	43.3	31.6	9.4	104.8	427.7	35.5	237.7	44.7	118.2	0.50
987.0	32.6	22.5	6.1	89.2	321.7	29.5	191.4	33.2	157.4	0.71
997.0	44.9	33.0	7.4	118.8	436.7	34.2	236.9	43.8	134.7	0.61
1007.0	51.6	28.9	10.3	250.0	683.1	30.2	302.4	41.6	706.9	0.42
1017.0	42.6	26.2	6.0	199.0	553.0	28.3	250.4	37.3	647.8	0.52
1027.0	37.6	26.6	5.5	94.9	421.1	29.9	214.4	41.7	214.0	0.58
1037.0	40.2	29.6	9.0	90.6	410.4	32.4	221.9	43.4	154.1	0.63
1047.0	47.3	37.2	10.3	93.1	548.9	37.2	262.5	50.8	145.7	0.75
1057.0	37.1	27.7	8.4	81.2	358.8	31.9	211.9	40.1	134.7	1.19
1067.0	35.6	26.9	7.2	76.4	379.6	29.5	204.1	39.7	125.5	0.84
1077.0	38.2	26.1	7.6	73.2	392.5	29.5	204.0	39.7	134.1	0.68
1087.0	44.7	31.2	6.4	92.3	455.7	32.9	226.9	44.2	187.8	0.52
1097.0	58.1	40.9	5.4	173.2	678.5	41.0	304.0	55.8	572.0	0.49
1105.5	39.6	22.3	3.9	247.2	893.5	29.6	256.4	33.7	2470.8	0.49
1112.0	47.4	25.8	6.0	265.3	819.1	29.7	292.3	38.8	3182.6	0.27
1118.5	41.5	22.8	7.8	261.8	889.1	28.8	272.1	35.6	3002.3	0.22
1127.0	30.8	21.5	4.5	89.5	351.6	26.6	167.9	32.0	280.5	0.42
1137.0	36.0	22.3	6.1	74.9	365.7	25.0	176.1	34.2	129.3	0.94
1147.0	32.8	23.2	7.3	74.5	353.4	26.3	184.0	33.9	93.1	0.74
1156.0	42.1	27.9	7.5	84.9	430.0	30.7	217.0	41.3	87.6	0.40
1161.0	42.5	30.4	5.9	102.3	435.9	32.8	248.6	45.2	353.5	0.39
1171.0	36.9	26.4	4.2	82.1	374.1	28.1	216.2	39.8	120.5	1.06
1181.0	28.3	19.1	5.4	54.7	291.8	21.8	154.7	30.1	111.8	1.71
1191.0	32.4	23.2	6.1	62.4	333.9	24.7	174.5	34.6	192.7	1.63
1201.0	46.2	32.4	6.7	98.0	517.4	33.8	255.0	49.3	160.7	1.03
1211.0	53.3	38.1	6.3	102.4	547.7	38.7	276.8	57.9	134.3	0.94
1221.0	59.6	42.8	11.6	114.3	583.7	43.5	312.8	63.6	102.3	1.10
1236.0	46.3	32.6	6.0	86.4	459.9	35.7	254.6	49.8	126.3	0.58
1246.0	60.7	45.7	10.6	114.1	610.7	46.2	337.8	69.5	129.6	0.56
1255.0	50.6	39.0	8.4	97.7	528.9	38.0	280.1	54.8	138.8	0.50
1264.0	49.6	34.9	8.6	95.8	510.7	37.2	273.4	53.6	211.0	0.60
1274.0	48.1	35.1	9.0	96.8	488.6	35.9	271.4	54.7	174.9	1.00
1281.0	67.2	48.0	8.9	124.8	822.3	47.0	371.0	74.3	258.2	0.82

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1288.0   51.5  36.9   8.4 113.8  553.3  36.8 286.9   58.0  379.5 1.09
1298.0   48.5  35.2   7.3  98.8  518.9  36.4 262.7   56.0  129.1 1.40
1308.0   63.9  52.2   9.4  93.5  702.3  41.5 309.4   69.3  128.6 1.08
1320.0   70.6  56.1  11.0 128.0  829.2  44.5 380.8   76.3  222.6 0.65
1327.0   46.6  31.7   6.6  98.1  512.3  30.0 222.9   48.2  341.9 1.19
1335.0   47.6  35.1   9.4  80.0  497.2  33.3 241.3   55.6  118.3 1.35
1344.0   56.4  39.4  11.4  92.9  587.8  40.9 273.6   63.9  373.4 1.30
1349.0   48.2  36.0  12.3  99.1  525.9  35.3 260.1   55.9  413.3 2.02
1359.0   35.3  25.1   3.3  63.4  366.7  24.3 180.3   39.1  181.5 3.52
1369.0   55.6  42.1  10.3 100.2  619.9  37.2 289.2   59.7  183.9 1.80
1379.0   48.5  35.5   8.2  83.4  524.2  34.5 253.1   53.8  136.5 4.39
1389.0   51.6  38.1  10.7  97.4  624.3  38.3 267.6   59.9  288.6 2.27
1398.0   64.9  47.6  12.6 135.1  832.5  41.9 335.1   73.0  744.1 1.25
1410.0   68.2  51.2  11.6 152.3  720.8  45.9 367.4   76.8  568.4 1.50
1420.0   78.4  59.9   8.0 172.9  851.9  53.2 411.4   89.8  467.5 0.32
1430.0   65.3  46.5   9.4 204.2  714.4  44.7 364.7   70.8 1275.9 0.19
1438.5   49.7  31.7   8.1 279.6  433.4  32.1 327.2   47.1 4153.4 0.11
1446.0   45.6  29.2   9.4 270.8  392.2  29.4 313.4   42.7 3993.6 0.10
1453.0   47.2  29.4   7.2 289.5  389.1  29.9 324.6   45.7 4524.8 0.13
1464.0   48.2  35.2  10.4 114.1  550.4  36.1 259.1   55.4  470.0 1.89
1475.0   60.2  43.7  10.6 107.8  785.1  42.6 305.7   70.0  241.7 1.17
1486.0   74.1  55.9  10.8 107.9  979.1  49.9 354.4   83.8  158.2 1.16
1496.5   77.0  58.9  14.4 103.9  932.3  52.0 368.9   88.9  147.7 1.38
1507.0   69.8  51.0  11.9  84.5  911.3  44.7 316.5   77.0  121.8 2.27
1517.0   65.9  47.2  13.4  92.1  809.7  42.9 317.2   75.6   96.0 3.03
1527.0   80.0  57.5  11.2 112.9  901.1  53.7 382.3   93.7  114.1 1.87
1537.0   76.0  56.4  13.2 106.8  903.7  54.0 372.4   92.5  107.8 1.07
1595.5   61.0  45.8   9.8 164.5 1066.4  37.5 302.3   70.9 1063.9 1.33
1605.5   65.9  50.9  10.4 176.0 1099.1  44.3 336.4   78.9  768.6 1.02
1618.0   56.5  39.6  11.7 142.9  840.0  42.4 285.1   68.2  527.2 2.21
1627.0   88.6  68.4  12.8 128.6 1259.7  55.6 417.9  105.2  172.1 0.64
1636.5   58.6  47.4  11.5 100.3  970.2  43.7 306.2   71.4  212.9 2.60
1645.5   34.4  23.6   7.5 181.9 1123.1  28.2 236.0   41.3  770.7 0.97
1654.5   47.8  39.1   9.4  78.3  780.8  34.4 261.2   63.1  105.0 3.94
1664.5   53.0  45.4   9.3  86.7  877.1  37.8 295.9   71.9  116.6 1.84
1674.5   34.5  21.4   7.3 240.0 1168.7  28.3 247.1   39.9 1300.1 0.52
1685.0   44.0  38.4  12.7  59.9  818.9  33.1 230.7   58.9   98.3 3.49
1695.0   61.7  53.4   9.7 102.6  925.3  41.4 346.6   83.8  138.8 1.24
1704.0   31.3  23.3  10.0  36.9  661.3  29.0 190.6   45.8   45.6 3.05
1727.0   72.8  57.7  13.2 105.1 1566.2  44.5 355.1   80.6  195.3 0.78
1746.0   35.2  26.6  12.3  69.3  534.3  26.4 187.6   44.6   95.2 6.62
1756.5   58.0  45.3  13.3 154.6  923.7  39.1 311.5   73.4  175.6 4.46
1765.5   33.6  28.1  12.5  53.3  816.4  21.0 168.1   40.5  108.5 5.13
1774.5   36.9  29.2  13.6  49.6 1073.3  21.5 176.9   40.8   97.5 4.38
1783.5   11.3   6.8  15.8  18.5  630.2   9.0  68.3   16.2   61.1 7.82
1794.0   20.1  16.4  13.8  33.9  762.3  13.8 107.9   26.5   58.6 5.89
1804.5   10.1   5.6  13.0  18.3  496.9   8.1  65.2   15.0   32.0 6.15
1821.5   48.9  36.8  11.8  86.0  888.4  37.4 260.3   62.6   95.8 3.18
1832.0   60.4  46.6  14.3 102.4  767.9  45.0 324.9   77.7  116.7 5.44
1842.0   76.1  60.1  15.9 117.0 1000.7  55.6 410.0   99.2  152.8 2.39
1851.0   76.8  55.1  16.1 114.9 1219.8  49.5 362.1   89.7  144.3 2.60
1860.0   60.4  41.8  14.0  87.6 1358.9  37.8 268.5   66.4  108.2 1.55
1869.0   62.5  40.0  13.1  82.7 1469.2  35.6 252.4   64.7  107.8 1.22
1878.5   84.9  55.3  19.7 103.6 1439.0  44.2 339.5   88.4  104.3 1.02
1888.0   76.2  53.0  16.9  97.4 1482.3  42.3 316.2   78.4  184.0 0.61
1898.0   96.2  60.0  16.5 101.1 1582.5  47.9 351.6   92.2  115.6 0.35
1909.0  101.9  66.8  19.9 109.8 1773.4  50.5 396.8  105.1  125.3 0.33
1929.0   86.6  57.4  16.5 136.4 1665.0  44.6 355.5   84.9  564.9 0.44
1940.5  108.6  67.9  18.2 114.5 1739.9  51.0 387.7  103.5   99.3 0.31
1949.5  112.9  72.2  15.2 140.6 1860.9  51.1 417.8  105.8  194.8 0.29
1959.0  107.6  64.9  13.0 149.1 1751.9  48.7 388.2   97.3  306.9 0.33
1969.0  125.0  74.2  15.9 128.1 1761.2  53.9 423.7  112.8  119.8 0.30
1979.0  111.7  69.6  12.9 135.9 1842.0  52.2 408.1  101.9  127.1 0.29
1988.0  108.5  63.1  13.4 130.4 1757.4  51.9 408.1   99.4  110.1 0.33
1997.5  121.1  70.3  17.3 136.9 1771.5  53.2 413.6  105.5  118.1 0.31
2006.5  126.4  72.2  13.3 139.6 1736.8  51.6 415.6  107.9   96.2 0.32
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2015.5  125.1  67.3  14.7 140.5 1770.3  53.7 423.6  105.9  115.1 0.42
2026.0  130.5  70.5  14.6 142.1 1724.1  51.0 416.9  107.0  109.5 0.37
2035.0  125.3  67.4  15.5 137.4 1583.5  54.3 409.3  105.0   97.4 0.43
2044.0  132.8  70.1  14.0 142.0 1620.8  52.7 413.7  107.8   79.5 0.43
2053.5  122.3  65.7  14.5 141.9 1724.9  51.5 411.7  102.2   92.8 0.45
2064.0  143.0  68.1  16.5 141.2 1655.5  54.2 403.4  108.4   79.3 0.45
2080.0  134.0  66.1  11.3 137.6 1710.1  52.4 402.0  103.9   79.5 0.57
2096.0  132.5  64.8  14.6 139.4 1786.2  50.8 393.4  102.2  100.7 0.66
2114.0  140.7  70.9  14.7 161.7 1817.2  51.9 395.7  106.8  151.9 0.40
2239.5   85.8  49.6   9.9 122.4 1427.5  43.1 345.4   81.4   90.8 1.60
2248.5   50.5  38.3  14.3  78.2 1056.5  34.1 244.3   57.1  215.4 0.35
2258.0   27.7  23.7   6.3  74.2  336.0  20.8 173.1   34.9  449.9 0.57
2267.0   34.4  28.4   6.0 123.3  340.1  27.8 243.9   44.5 1170.7 0.46
2276.0   40.1  33.2   7.0  78.6  615.6  28.4 230.4   49.9  340.6 0.60
2285.5   17.7  12.8   4.6  26.3  263.5  14.8  87.1   21.0   65.8 0.59
2294.5   16.9  14.4   8.5  28.8  297.0  15.0  90.7   23.0   56.1 0.70
2303.5   40.3  34.0  14.3 156.8  606.7  25.9 233.7   42.2 1203.1 0.89
2313.0   40.6  33.5   6.7  92.5  609.9  27.5 232.9   52.1  469.0 0.64
2349.5   66.5  50.6   9.7 144.3 1152.3  46.7 375.1   79.0  527.2 0.47
2360.0   64.7  49.9   8.1 134.1 1065.7  47.2 359.0   79.3  298.3 0.56
2370.0   48.2  38.5   7.3 139.8  693.5  40.2 341.6   62.7  852.9 0.76
2379.0   58.2  45.5   8.3 131.4  787.9  44.2 338.2   71.6  411.8 0.73
2389.0   68.2  51.6   9.5 129.5 1029.0  48.5 360.6   82.1  274.1 0.79
2399.0   71.3  55.8   9.5 134.0 1155.6  47.1 358.6   82.1  327.7 0.68
2413.5   74.6  59.8  12.4 147.6 1214.9  50.0 405.3   91.9  447.8 0.39
2423.0   73.5  57.9  12.8 147.9 1035.0  52.3 421.2   94.3  539.4 0.34
2432.5   80.9  65.4  13.0 160.4  956.9  58.1 461.7  105.4  591.3 0.24
2445.5   69.2  56.2   9.1 227.4  702.1  52.4 482.5   91.7 1725.2 0.21
2457.5   59.9  50.6  10.6 294.4  470.4  49.6 503.9   87.3 3401.0 0.10
2470.0   49.4  43.3  14.6 347.3  336.1  44.3 487.8   76.3 4076.9 0.38
2480.0   73.8  60.5  13.6 241.7  842.0  53.5 503.4   99.0 2653.7 0.39
2490.0   71.5  58.4  12.0 229.5  713.1  53.9 484.2   95.5 2309.4 0.23
2499.5   59.8  49.2  10.0 157.6  742.6  42.8 364.8   75.9 1129.3 0.58
2508.5   48.6  39.1   9.7 128.2  619.0  34.4 299.0   63.0 1198.7 0.41
2518.0   51.2  42.7  10.4  90.0  758.1  34.4 285.0   62.0  259.0 0.45
2527.0   53.0  44.4   9.8 100.6  821.7  38.1 315.6   68.2  318.4 0.50
2549.5   44.4  34.2   6.0  86.8  612.6  30.2 238.7   55.1  199.9 0.46
2561.0   49.8  38.8   7.9 105.7  888.3  32.2 254.0   55.7  607.8 0.45
2570.0   34.6  24.6  11.0  50.7  539.8  23.2 179.1   42.1  149.2 0.37
2579.0   63.7  48.3   6.5  75.1 1170.5  37.7 295.6   71.3  159.6 0.57
2588.0   63.6  52.6  12.7  91.9 1133.8  42.4 334.5   76.8  291.9 0.55
2609.5   87.3  66.6  16.3 102.8 1378.2  52.1 392.1   98.6  198.9 0.13
2620.0   70.4  57.0  10.7 133.4  857.2  49.0 402.1   89.4  599.3 0.25
2631.5   74.3  64.8  15.8 203.8  804.0  55.5 512.7  104.0 1940.1 0.51
2645.0   50.5  38.9   6.2  94.4  614.4  36.1 276.6   61.9  224.9 0.67
2654.0   64.4  52.4   7.9 128.2  924.4  43.9 356.9   76.5  920.5 0.33
2663.5   42.9  34.3   6.8 125.8  484.8  31.9 271.3   54.3  921.1 0.45
2672.5   35.6  29.6   7.6  77.8  483.7  27.5 219.6   43.3  518.4 0.24
2681.5   39.8  32.5   6.7  66.7  549.0  27.4 215.8   49.6  151.7 0.36
2690.5   42.6  35.1   5.9  64.2  627.5  29.2 230.4   53.3  181.5 0.44
2699.5   27.5  25.4   3.7  48.8  471.9  22.3 173.3   38.2  157.7 0.29
2708.0   31.1  25.8   9.1  57.5  506.3  25.2 197.9   42.1  233.3 0.38
2717.5   30.3  26.0   4.2  47.2  434.1  22.3 169.9   38.9  165.2 0.49
2729.0   35.7  29.5   7.8  50.9  498.6  23.6 181.7   43.5  160.9 0.78
2748.0   31.0  25.9   6.7  50.3  493.2  23.0 175.7   39.9  120.3 0.86
2826.5   44.3  35.3   6.1  70.8  635.2  28.1 234.9   50.8  219.9 0.66
2855.5   42.6  33.9   7.5 114.1  415.4  30.4 261.0   54.7 1488.3 0.50
2874.0   29.3  23.4   5.5  58.5  448.9  20.8 173.3   33.9  301.6 0.71
2883.0   19.6  14.2   8.2  30.3  272.1  19.1 123.9   25.8   36.3 0.58
2892.5   31.7  27.8   5.0  55.5  394.1  22.9 185.9   43.0  126.9 0.78
2902.0   42.3  37.6   7.7 103.1  459.2  30.3 268.6   56.9  870.7 1.04
2911.0   39.7  34.2   6.1 101.7  457.0  30.4 257.5   54.6  778.7 0.74
2920.5   62.9  54.0   9.7  86.4  985.2  39.8 334.1   72.1  269.1 0.63
2930.5   46.6  38.9   9.6  94.2  581.6  34.4 275.5   62.0  199.0 0.81
2952.5   70.5  57.8  12.0  99.2 1073.5  42.0 334.5   78.9  180.8 0.49
2964.0   45.0  35.3   7.6 102.3  547.8  32.5 253.2   55.9  345.7 0.66
```

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2976.5   30.5   23.5    4.3   80.1   369.1   24.4  190.2   39.9   349.6  1.12
2989.5   28.5   24.2    5.7   52.5   415.6   22.5  167.0   38.3   128.4  0.84
3000.0   27.4   23.9    6.8   51.6   414.6   22.4  165.2   36.1    98.5  0.77
3011.5   21.4   18.3    5.5   38.8   319.5   18.5  121.6   27.7    72.9  1.00
3021.5   16.0   14.1    4.0   32.0   229.8   13.8   99.3   23.0    53.0  1.15
3031.5   11.4   10.8    5.3   30.2   193.7   11.6   85.6   19.9   113.4  1.02
3044.5    9.2    8.5    8.2   19.3   174.4    7.1   57.7   14.0    54.6  1.41
3056.0   13.0    8.7   14.3   24.6   344.3    9.9   76.8   17.7    37.2  1.09
3067.5   12.8    7.0   10.2   23.7   195.0   11.7   81.3   16.8    34.1  0.94
3078.0   26.4   22.5    5.5   41.3   350.6   16.9  144.0   34.3    78.7  1.62
3088.0   36.6   29.4    7.0   65.0   481.0   27.1  204.3   45.9   152.5  1.33
3098.5   49.3   38.0    9.1   90.9   685.6   34.2  263.6   58.3   151.3  0.90
3110.0   51.4   39.6    9.7  104.4   690.1   35.8  286.7   60.1   301.2  0.99
3122.0   53.9   41.8    6.8  114.4   671.4   39.4  317.0   67.2   196.0  0.72
3155.5   46.4   33.9    6.5   93.7   606.5   33.3  274.7   58.7   289.4  0.76
3166.0   46.6   38.5    9.3  124.1   478.9   32.5  298.2   60.2  1295.4  0.70
3176.5   37.9   31.6    8.2   64.7   477.1   27.3  216.3   48.7   150.6  1.10
3187.0   29.9   23.1    7.5   54.5   390.4   23.8  189.3   41.0   111.7  0.86
3197.0   23.5   17.0    8.4   40.8   339.8   20.1  151.8   31.1    86.8  0.99
3207.0   29.4   24.2    3.3   53.5   418.2   19.8  167.8   35.9   185.2  0.88
3217.5   45.5   36.1    7.3   74.3   598.2   30.9  238.4   52.0   157.8  0.71
3226.5   50.0   41.6    9.1   74.2   618.6   32.6  246.8   54.3   161.6  0.78
3236.5   34.2   28.9    7.4   63.5   498.0   24.5  189.9   40.9   250.2  0.75
3249.5   29.7   23.9    4.9   51.8   380.8   21.4  176.6   38.2    91.0  1.19
3258.5   34.8   27.3    6.3   57.5   502.4   29.3  205.6   42.9   130.7  0.98
3268.0   30.7   25.2    5.2   52.1   414.0   21.7  178.7   38.1   106.2  0.84
3277.0   31.5   25.6    4.6   61.8   466.2   24.8  204.7   42.4   221.8  0.79
3286.5   24.5   21.5    2.5   70.4   405.3   23.6  201.6   35.3   624.8  0.68
3297.5   37.7   31.1    7.3   99.8   535.8   27.2  230.9   44.7  1185.9  0.61
3307.5   25.2   20.7    3.8   33.1   387.4   16.0  127.1   27.8    96.9  0.77
3317.0   11.1   10.0    0.6   23.4   166.4    9.9   72.4   15.6    70.0  0.99
3326.0   20.5   16.0    2.3   52.5   281.9   15.4  130.3   25.1   304.4  0.90
3337.0   15.5   13.8    1.1   34.0   243.7   12.5   97.5   21.0   136.1  0.88
3356.5   13.1    9.0    1.0   19.7   171.2    8.2   66.4   15.2    46.6  0.87
3367.0   12.7   10.4    3.1   21.8   211.6   10.8   76.4   16.8    75.2  0.96
3378.5   28.8   24.5    4.8   41.5   513.7   17.0  139.4   31.0   157.7  0.81
3390.0   10.5   10.6    3.4   30.5   160.7    9.0   81.2   17.2   276.4  1.17
3402.5   10.5    9.1    3.2   16.1   171.0    6.8   61.9   15.1    63.6  1.28
3412.0   12.8   12.0    1.5   24.3   237.5   14.7   88.9   19.5    81.8  1.07
3422.5   20.6   15.7    1.7   33.1   297.4   13.3  109.1   25.3   164.2  1.02
3433.5   25.0   18.6    2.4   39.2   386.0   16.7  131.2   27.7   150.3  0.91
3444.0   37.0   27.6    4.9   78.4   371.6   26.5  201.2   46.5   830.0  0.85
3454.0   56.0   44.5   11.4   78.1   736.5   36.2  265.0   67.5   216.1  0.86
3464.0   45.7   35.7    9.0   54.5   727.8   29.4  218.6   56.0   121.5  0.82
3474.5   47.4   39.4    8.4   76.5   637.6   29.8  240.3   57.6   153.9  0.85
3485.0   52.0   43.3   11.2   74.6   921.1   32.0  262.1   62.1   180.1  0.72
3495.5   43.3   33.6    6.7   75.3   632.3   28.6  237.5   52.2   172.2  0.72
3504.5   46.2   34.6    8.8   85.4   672.8   34.5  249.2   56.9   174.7  0.84
3514.5   47.5   35.6    9.5   88.4   731.4   33.9  254.6   56.9   291.5  0.74
3524.5   56.4   40.3    9.2  131.1   771.4   38.1  305.3   63.7  1041.6  0.45
3534.0   62.0   47.7   11.7   85.2  1052.2   39.1  295.9   69.7   133.0  0.42
3543.0   52.9   42.9    7.6   82.3   856.0   33.6  284.3   62.5   174.5  0.89
3561.0   43.0   35.6    6.5   70.0   659.2   29.1  229.8   53.9   143.9  1.06
3571.5   44.8   36.4    5.9   63.9   731.6   28.1  231.1   53.7   182.5  0.69
3581.5   32.0   25.3    4.5   44.8   459.1   21.7  176.6   42.6   127.6  1.04
3591.0   60.5   50.4   11.8   79.4  1120.7   35.2  282.8   70.2   212.4  0.58
3600.0   57.5   45.8   10.2  129.0   928.0   40.0  350.6   73.8  1158.3  0.61
3609.0   53.3   40.4    8.9  103.3   778.6   38.0  303.6   66.5   329.8  0.72
3619.5   57.7   44.0    9.0  100.7   804.2   39.2  307.2   68.7   277.4  0.43
3630.0   55.3   42.7    9.2  106.1   766.4   37.5  300.4   67.3   279.7  0.37
3642.0   47.8   37.0    7.5  106.3   577.1   36.0  281.5   59.1   312.8  0.44
3666.0   70.5   53.7   12.5   84.1  1126.9   41.1  319.4   78.8   192.3  0.52
3677.5   65.7   52.0   10.0   83.9   901.8   41.3  311.6   79.4   214.3  0.71
3705.5   62.4   46.6   10.1  111.9   732.1   37.8  303.2   69.3   648.5  0.52
3717.0   62.0   47.4    9.8   99.0   881.6   40.4  320.7   73.5   457.4  0.43
3727.5   65.1   50.5   11.0   99.0  1147.0   44.6  365.9   77.0   401.8  0.60
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3738.0   58.7   46.7    9.5   83.4   730.3   35.7  287.2   70.4   305.0  0.72
3768.0   70.5   60.0   13.8  135.0   909.3   46.4  388.4   85.3   927.9  0.59
3779.5   64.4   51.8   12.3  145.5   979.1   47.4  401.3   81.6  1126.8  0.47
3790.0   63.0   51.7   11.6  132.7   738.1   44.1  355.7   79.2   969.3  0.55
3800.0   66.2   51.5    9.0  104.2   795.7   41.9  329.5   80.8   520.4  0.71
3810.5   66.0   49.8    9.2   97.1   802.6   39.2  312.9   78.1   437.3  0.88
3854.0   57.2   44.8    9.9   78.6   832.7   35.8  274.3   68.8   266.4  0.86
3864.0   79.6   64.4   15.6  125.3  1322.0   48.3  412.7   95.9   694.4  0.56
3876.0   81.2   59.9   12.8  101.6  1267.8   49.5  390.3   94.5   190.9  0.65
3886.0   72.7   54.5   13.0   95.3  1097.0   45.4  348.8   87.2   303.7  0.63
3896.5   82.5   65.4   15.6  117.4  1714.1   48.7  408.7   93.4   273.0  0.34
3908.5   83.9   62.3   14.3  107.4  1303.9   50.6  396.7   97.7   163.7  0.59
3919.5   82.8   63.0   12.6  117.5  1254.6   51.2  398.8   97.8   217.9  0.42
3938.5   77.5   57.9   11.8  147.5  1032.5   53.6  426.5   93.5   842.2  0.41
3948.0   84.4   66.1   17.0   93.3  1224.9   50.9  389.9  100.5   120.2  0.78
3957.0   91.2   71.8   16.2  101.6  1277.2   54.6  430.9  110.2   141.6  0.54
3967.0   87.8   68.5   14.5   96.8  1117.6   52.6  393.8  101.1   127.0  0.55
3977.5   90.8   72.0   17.8  100.2  1154.0   53.7  408.3  105.8   109.3  0.45
3988.0   93.4   71.3   18.5   96.1  1285.4   55.0  427.3  110.7   123.6  0.27
3998.0   90.9   70.4   19.2   96.1  1241.3   55.1  428.2  110.0    95.4  0.31
4008.5  100.6   77.9   18.9  106.5  1414.7   59.4  462.1  120.2   125.7  0.23
4017.5   92.9   74.7   16.4  107.3  1286.5   57.3  450.6  114.3   145.0  0.33
4029.0   91.7   71.6   15.6  101.5  1425.3   57.1  445.7  110.4   155.5  0.34
4052.0   81.8   64.3   13.3   98.6  1276.5   48.7  396.9   98.8   192.8  0.33
4062.5   68.4   50.4   11.5   97.2  1125.2   44.0  353.0   79.6   221.7  0.45
4073.0   63.4   50.8   14.1  123.7  1008.4   44.2  348.7   78.5   507.1  0.40
4083.5   74.3   55.2    9.0  136.9  1112.5   47.8  391.7   88.6   630.5  0.59
4097.0   84.6   64.2   16.0   98.3  1362.9   48.3  384.0   97.1   152.9  0.73
4106.5   73.0   55.3   12.9   96.1  1133.4   41.6  344.0   86.0   168.3  0.93
4120.0   64.3   48.5   11.2  136.4  1002.2   42.9  365.9   79.4   608.8  0.74
4130.5   68.0   50.1   11.9  135.3   965.1   43.2  349.3   80.1   599.2  0.73
4139.5   66.9   47.4   10.6  108.1  1050.9   40.9  322.2   78.0   126.8  0.61
4149.0   62.3   46.9   14.1  107.9   966.7   43.7  328.4   75.2   105.7  0.38
4158.0   76.3   56.7   12.6  113.8  1253.1   46.8  365.1   88.0   118.1  0.52
4167.5   74.9   56.3   11.8  115.3  1175.2   46.6  362.8   87.6   125.1  0.50
4176.5   80.7   59.0   10.7  120.7  1176.3   51.1  387.2   94.8   135.4  0.41
4185.5   75.1   54.6   15.3  106.5  1203.8   48.2  366.2   85.5   111.2  0.29
4210.0   76.0   56.2   13.4  115.3  1205.7   47.5  385.4   89.9   146.2  0.51
4220.5   69.3   53.9   10.3  116.7  1436.3   44.9  367.9   81.7   261.7  0.55
4231.0   42.7   29.7   14.6   86.6   632.8   34.5  260.7   53.8    82.6  0.25
4241.0   63.5   47.2   11.0  103.4   965.9   43.3  330.2   77.5   133.6  0.52
4251.5   62.1   47.3   12.4  104.6  1006.5   47.4  376.1   79.0   136.5  0.66
4262.0   65.5   50.6   12.8  112.5   890.2   44.4  337.4   80.4   178.8  0.59
4272.5   53.8   38.1    9.9  102.3   664.9   37.6  280.2   62.9   178.4  0.55
4281.5   73.3   54.0   14.7  111.3  1049.0   49.5  380.7   86.7   169.5  0.83
4290.5   67.0   49.3    9.5  119.7   824.5   43.7  344.5   80.5   196.9  0.43
4303.5   61.2   45.9   10.7  104.1  1001.0   46.1  379.5   81.9   160.7  0.79
4312.5   60.1   45.6   11.9  109.0   834.4   45.2  350.6   77.6   184.4  0.51
4323.0   77.3   57.3   13.0  119.5  1065.8   54.1  405.3   94.3   159.3  0.33
4333.0   75.6   55.0   12.2  120.2  1133.4   47.4  368.5   86.7   185.8  0.36
4342.0   61.7   46.3   10.4  121.7   910.8   41.8  338.5   75.0   388.2  0.46
4351.0   49.6   34.4   17.1   93.1   868.2   39.0  318.9   61.1   248.4  0.30
4361.0   65.4   47.4   11.4  138.2   863.8   41.6  336.2   76.0   747.2  0.47
4371.0   64.3   46.9   10.5  113.4   879.7   42.9  315.6   72.7   156.1  0.56
4380.0   49.0   36.8    6.5   97.4   662.3   34.8  263.9   58.6   193.7  0.76
4390.0   48.6   36.4   10.6   91.1   708.6   34.7  264.3   58.4   193.7  0.79
4412.0   75.7   56.4   12.5  104.2  1178.8   45.1  363.4   84.0   186.1  0.76
4421.0   60.8   47.3    8.3   98.7   824.9   40.5  324.2   73.1   362.7  0.71
4437.5   74.7   57.4   11.6   94.5  1111.2   43.2  344.5   83.0   169.4  0.73
4446.5   67.9   53.1   12.2  100.8   972.5   43.4  345.1   78.5   218.2  0.76
4456.0   62.1   46.2    8.1  130.9   904.6   40.6  339.6   71.9   927.2  0.40
4465.0   56.1   41.9    6.4   95.6   715.0   41.4  291.7   63.8   151.7  0.46
4473.5   54.7   42.6    8.4  106.1   685.6   39.2  288.6   62.6   280.3  0.61
4486.0   57.0   43.6    9.0  100.3   872.6   43.4  339.0   67.6   158.6  0.74
4496.0   58.0   44.7    7.5  101.9   773.3   42.0  327.1   67.7   177.0  0.43
4509.5   59.0   44.7   10.0   98.6   760.0   39.4  308.1   67.6   210.9  0.58
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4519.0  59.4  46.5   9.9 108.8   762.5  42.8 341.7  72.4  263.4 0.46
4528.0  56.6  44.0   9.8 103.2   778.2  44.7 338.5  69.5  253.7 0.41
4548.0  54.5  42.1   8.0  91.1   890.1  42.0 347.2  66.6  142.3 0.83
4556.0  65.6  50.0   6.9 104.4   903.6  47.2 365.8  78.0  162.3 0.56
4564.0  65.1  49.7   8.4 116.0   845.5  44.0 344.1  73.3  176.7 0.40
4577.0  65.3  51.1   8.9 112.6  1002.0  49.1 408.5  78.0  293.1 0.44
4588.0  60.2  44.5  10.3 122.7   901.0  42.1 328.3  68.7  391.6 0.34
4597.5  59.6  46.7  10.1 116.4   866.4  44.2 345.5  72.4  159.7 0.30
4607.0  75.9  58.3  14.5 130.9   958.8  52.0 412.1  93.3  200.6 0.28
4618.0  63.7  50.1  10.0 129.8   825.8  46.5 367.3  76.7  416.2 0.34
4630.5  47.3  37.1   7.2  92.6   671.6  36.7 272.0  57.7  132.5 0.59
4641.0  55.7  42.3   7.3 101.5   762.4  36.5 293.5  63.1  132.8 0.49
4651.0  49.8  37.7   8.1  94.5   671.5  34.9 274.3  58.6  122.0 0.46
4661.0  42.2  33.0   8.8  82.9   772.1  41.0 313.3  52.9  134.7 0.69
4671.5  38.8  32.4   6.1  79.7   522.3  28.4 225.4  45.8   92.9 0.59
4681.5  59.0  45.4   9.6 102.9   787.2  40.1 307.4  66.8  125.9 0.41
4691.5  57.9  46.6  12.8 100.7   887.3  47.5 416.6  80.0  172.2 0.87
4710.0  59.2  46.0  11.2  96.2   985.3  41.0 329.2  68.1  218.3 0.58
4718.5  48.0  36.8   7.5  90.2   752.8  34.1 256.5  57.6  108.0 0.47
4730.0  51.7  42.0   8.0  88.9   932.4  35.7 275.3  61.4  170.9 0.58
4740.0  61.4  46.7   9.3  95.7  1094.0  40.8 307.1  67.9  293.3 0.59
4751.5  51.3  42.6  10.8 152.8   599.8  41.5 351.4  66.6 1816.7 0.49
4763.0  48.9  39.2   6.6 161.1   500.3  35.4 341.7  63.7 1946.2 0.46
4773.0  59.9  45.6  10.1 109.2   740.0  43.4 352.2  71.6  148.4 0.69
4822.5  78.7  63.1  16.8 102.4  1141.3  45.6 399.3  86.6  169.8 0.45
4839.0  67.1  56.9  10.8 101.2  1193.5  46.0 391.5  84.2  108.2 0.31
4849.5  73.0  60.9  11.1 105.0  1103.1  46.8 369.0  87.1  124.6 0.43
4859.5  61.5  49.0   9.7  99.1  1057.5  37.5 321.8  69.9  224.9 0.54
4870.0  36.8  27.9   5.9  61.0   495.6  28.3 203.4  47.9   93.7 0.89
4880.0  46.4  38.6   9.1  64.6   785.0  27.5 224.2  50.3  135.4 0.85
4893.0  35.2  27.9   6.3  48.7   581.0  22.8 203.6  41.3  129.2 1.46
4902.5  24.2  19.4   2.9  44.4   403.2  23.6 153.4  34.7   96.3 0.67
4913.0  25.7  21.3   6.2  46.7   495.1  19.1 153.8  33.0  142.0 1.01
4923.5  15.4  12.7   4.7  30.4   248.7  12.5  90.9  19.8  109.6 1.04
4933.0  22.4  17.7   5.3  41.5   385.5  18.7 128.1  28.8  124.8 0.86
4943.0  42.8  35.3   8.9  66.0   696.7  26.4 221.7  48.5  225.7 1.25
4953.5  44.3  38.8   6.8  63.4   651.9  25.6 223.4  53.2  123.6 1.08
4962.5  49.5  39.9  11.5  77.8   655.2  38.9 266.9  60.0  141.7 0.63
4971.5  64.4  53.1   9.6 123.9   733.6  39.4 358.2  79.8  203.9 0.50
5006.5  55.7  45.6   6.7  95.6   864.5  37.5 303.1  67.9  160.1 0.66
5015.5  54.0  42.3   9.9  97.2   880.5  42.9 334.5  67.3  147.5 0.53
5025.0  69.4  54.5   8.8 106.5  1249.1  40.8 342.9  76.2  215.0 0.50
5034.0  69.6  54.9  14.7 104.6  1226.3  44.8 348.9  81.5  170.6 0.56
5043.0  80.0  63.9  11.7 116.7  1177.2  51.8 412.8  95.0  443.7 0.35
5052.0  88.2  70.4  12.3 116.5  1216.4  54.5 438.7 104.8  419.0 0.31
5061.0  86.8  70.3  16.1 161.4  1160.8  54.5 474.0 105.1 1854.1 0.14
5070.0  97.4  79.8  14.1 100.6  1433.5  55.4 470.7 115.6  104.4 0.14
5079.0  84.7  70.1  11.8  96.1  1404.2  49.3 451.6 101.5  163.3 0.33
5089.0  69.9  53.6  12.2  93.1  1051.1  47.4 346.5  83.9  159.5 0.37
```

depth	Ctot	Ntot	Sulp	Cinorg	LOI	water	I	Br	Mo
5.0	6.77	0.64	0.70	0.000	14.26	69.5	2.6	23.3	4.2
15.0	21.57	1.95	2.50	0.037	44.06	85.6	5.5	86.3	5.7
25.0	21.03	1.60	2.30	0.932	43.90	82.0	10.4	78.7	3.1
35.0	18.94	1.50	2.14	1.119	38.96	82.2	9.9	79.9	5.2
45.0	17.58	1.52	2.54	0.103	38.34	86.2	4.5	79.9	8.2
55.0	13.50	1.15	1.34	0.034	30.39	90.0	2.3	55.5	7.2
65.0	11.02	0.93	1.72	0.000	26.92	89.5	-5.0	44.4	7.6
75.0	14.58	1.28	2.32	0.000	33.80	87.5	6.4	53.8	7.1
85.0	16.83	1.45	2.26	0.000	38.45	87.8	6.3	61.0	10.0
95.0	13.62	1.18	3.01	0.000	35.80	86.9	5.5	50.8	8.2
105.0	7.05	0.72	0.96	0.000	17.10	86.6	2.6	30.2	7.3
115.0	2.05	0.23	0.41	0.082	5.36	57.6	-1.7	10.6	4.6
125.0	14.36	1.31	1.43	0.000	31.06	89.4	1.3	60.7	7.5
135.0	13.03	1.17	1.42	0.000	29.72	91.2	6.8	50.8	7.3
145.0	13.01	1.18	3.35	0.000	29.31	91.6	3.1	52.3	6.8
155.0	15.35	1.34	1.45	0.000	32.83	91.5	3.4	49.6	5.3
165.0	14.35	1.24	1.39	0.000	31.15	91.2	2.5	45.5	4.5
183.0	16.75	1.79	1.94	0.000	34.65	91.6	3.1	48.3	6.2
193.0	18.24	1.87	1.79	0.000	36.37	91.6	3.9	51.8	6.2
203.0	15.03	1.66	1.66	0.000	31.81	92.5	8.5	55.5	6.3
213.0	13.58	1.40	1.66	0.000	29.42	91.4	6.3	51.7	5.5
223.0	16.67	1.87	2.43	0.000	37.05	89.6	5.9	53.9	6.6
233.0	15.33	1.75	2.50	0.000	35.04	88.4	10.4	59.2	7.8
243.0	14.47	1.65	2.51	0.000	31.64	85.8	7.2	48.4	7.1
253.0	17.24	1.87	2.43	0.000	37.86	87.6	6.3	63.2	5.8
263.0	17.17	1.83	2.07	0.000	36.87	88.2	2.4	62.7	7.5
273.0	21.58	2.18	2.61	0.000	44.35	88.1	5.0	71.1	11.4
283.0	22.37	1.94	1.98	0.000	44.44	87.7	2.0	57.7	13.4
293.0	19.79	1.82	1.22	0.000	39.55	87.9	3.9	51.8	8.6
303.0	15.10	1.52	1.57	0.000	33.09	87.5	5.6	56.1	10.1
310.5	11.21	1.28	2.37	0.000	22.80	85.5	5.2	42.0	15.1
315.5	1.33	0.54	0.22	0.000	4.28	43.2	2.3	8.7	5.5
320.5	0.64	0.48	0.41	0.000	3.23	37.8	2.2	3.9	4.4
327.5	14.71	1.46	1.10	0.000	29.82	88.3	8.7	45.4	10.3
335.5	0.65	0.42	0.29	0.085	3.50	30.9	-1.0	4.0	2.3
343.0	21.24	2.38	2.26	0.000	42.67	89.4	4.7	69.7	15.1
353.0	16.17	1.77	1.62	0.000	34.23	88.5	11.3	49.6	11.3
362.5	24.20	2.44	2.13	0.000	49.55	87.2	5.5	65.2	16.9
377.0	15.19	1.73	1.22	0.000	30.96	82.6	6.5	44.8	12.2
387.0	28.11	2.75	1.81	0.000	54.79	87.4	2.2	81.3	19.6
397.0	22.57	2.18	1.85	0.000	47.27	86.4	8.5	64.8	16.8
407.0	26.07	2.55	2.62	0.000	38.59	87.3	6.4	61.2	19.4
417.0	30.10	2.75	4.23	0.000	59.28	86.7	9.5	78.5	26.2
427.0	26.98	2.62	2.92	0.000	51.90	85.0	9.3	80.7	21.8
437.0	24.05	2.44	2.16	0.000	44.52	87.3	4.1	79.6	14.7
447.0	15.58	1.68	1.64	0.000	30.13	82.7	8.3	56.6	11.5
457.0	31.66	2.91	3.58	0.000	60.08	86.1	4.3	98.6	24.0
467.0	29.99	2.74	2.40	0.000	53.85	85.7	6.3	105.8	23.7
477.0	29.33	2.73	4.29	0.000	58.58	85.0	8.4	85.7	20.1
487.0	28.64	2.90	2.95	0.000	55.88	86.2	6.3	100.2	23.3
497.0	30.23	3.01	3.11	0.000	58.20	86.3	3.6	96.0	28.8
507.0	22.22	2.14	1.94	0.000	43.09	80.4	8.0	65.4	24.1
517.0	27.77	2.76	2.99	0.000	56.44	86.8	7.1	76.0	26.2
527.0	19.74	2.29	2.82	0.000	41.94	86.1	5.4	63.6	18.2
537.0	13.11	1.74	3.96	0.000	29.04	86.4	6.3	40.9	13.1
547.0	17.28	1.85	2.38	0.000	37.00	83.0	-0.8	63.5	20.7
555.0	19.29	2.06	2.37	0.000	40.78	83.3	0.8	80.3	32.3
562.0	20.92	2.15	3.17	0.000	45.44	82.6	6.3	65.0	37.2
577.0	18.70	1.87	3.05	0.000	40.30	82.8	9.5	50.4	25.9
587.0	23.47	2.38	2.97	0.000	48.44	85.7	7.2	109.1	28.7
597.0	24.45	1.97	3.27	0.057	48.19	84.3	9.9	127.3	27.6
607.0	20.72	1.73	5.97	0.035	42.98	83.6	1.9	68.0	31.4
617.0	15.26	1.52	2.96	0.029	35.96	82.8	12.4	58.8	26.5
626.0	6.99	0.84	0.96	0.361	17.31	66.5	7.3	24.3	11.8
634.0	15.65	1.73	2.39	0.108	34.68	82.9	5.9	53.8	21.1
642.0	10.13	1.01	1.48	0.298	23.56	74.1	1.8	29.4	16.9
649.5	1.37	0.39	0.86	0.190	5.22	43.4	6.1	5.7	5.5
657.5	6.09	0.83	2.15	0.105	14.83	63.2	5.4	18.4	10.1
667.0	17.33	1.68	5.23	0.000	35.06	80.1	8.0	36.0	18.5
677.0	10.34	1.16	3.44	0.000	23.58	73.6	5.5	25.1	14.0
687.0	30.39	3.02	6.48	0.000	58.85	87.6	2.5	60.2	29.1
697.0	27.73	2.57	6.60	0.000	53.89	85.8	9.7	101.7	36.1
707.0	22.28	2.30	5.55	0.070	47.51	84.7	6.4	100.7	37.0
717.0	16.13	1.61	5.25	0.091	42.08	83.7	6.7	61.2	35.5
727.0	17.84	1.84	4.95	0.000	39.12	82.3	3.9	71.6	42.3
737.0	15.92	1.51	3.49	0.000	34.57	80.6	6.6	65.2	40.4
747.0	10.02	1.24	2.75	0.000	23.66	75.2	12.5	38.9	26.3
756.5	10.06	2.07	2.93	0.000	21.23	73.6	6.4	31.7	22.7
776.5	8.60	2.06	2.36	0.000	16.50	68.6	4.0	24.0	16.9
785.0	2.47	1.04	1.04	0.000	6.47	48.5	2.9	11.5	7.2
794.0	13.58	3.00	3.72	0.000	24.85	82.1	0.3	41.8	27.8
804.0	13.97	2.19	3.79	0.000	29.82	78.3	6.7	42.6	38.5
814.5	14.92	2.06	4.37	0.000	32.79	79.5	9.6	42.4	39.2
825.0	18.95	2.06	6.18	0.000	43.75	83.6	9.4	49.1	74.2
835.0	17.82	2.47	5.69	0.000	39.47	82.9	13.3	43.2	92.6
845.0	13.81	1.34	3.60	0.000	29.21	77.4	6.1	40.3	82.9
855.0	10.60	1.21	2.73	0.000	23.46	75.6	2.9	31.2	50.3
865.0	4.12	0.72	1.70	0.000	11.39	60.6	6.0	18.7	22.6
877.0	6.64	0.85	2.02	0.000	15.21	67.8	6.6	26.5	27.0
887.0	6.17	1.04	2.13	0.000	15.08	67.8	-3.2	23.6	17.5
897.0	7.26	0.92	2.09	0.000	17.27	68.7	4.8	26.6	16.5
906.0	4.29	0.55	1.45	0.000	11.25	58.9	2.8	18.3	15.1
915.0	6.92	1.04	2.45	0.000	17.44	69.5	6.3	29.7	15.9
924.5	6.96	0.93	2.09	0.000	17.28	65.7	0.1	25.0	14.0
932.5	4.27	0.94	1.58	0.000	12.03	60.1	0.2	19.2	12.2
941.0	7.49	0.84	2.48	0.000	19.11	72.9	5.4	38.4	19.4
951.0	6.79	0.82	1.93	0.000	17.68	68.8	1.5	63.8	13.6
961.0	6.53	0.71	1.89	0.000	16.68	67.0	5.3	32.1	16.2
977.0	4.83	0.77	1.72	0.000	13.97	62.9	1.9	20.4	10.5
987.0	7.80	1.11	2.02	0.000	18.19	68.0	1.6	28.9	20.1
997.0	6.21	0.76	1.81	0.000	15.93	63.9	0.7	21.9	16.7
1007.0	2.09	0.64	1.09	0.000	6.89	45.7	6.7	7.8	10.4
1017.0	3.40	0.73	1.40	0.000	9.83	56.8	3.1	13.9	8.5
1027.0	5.32	1.09	1.28	0.000	13.68	63.5	6.4	23.4	7.3
1037.0	4.84	0.75	1.98	0.000	14.01	63.6	3.7	22.3	7.5
1047.0	4.94	0.81	1.38	0.000	14.75	62.2	6.1	23.1	7.5
1057.0	6.03	0.89	2.22	0.000	16.74	65.7	3.2	31.8	15.8
1067.0	5.68	0.74	1.59	0.000	15.71	65.3	4.0	33.9	13.5
1077.0	5.51	0.86	1.46	0.000	14.69	64.3	7.4	25.8	12.1
1087.0	4.77	0.75	1.31	0.037	13.55	61.8	5.6	18.1	7.9
1097.0	2.51	0.60	0.95	0.116	10.13	47.0	4.7	8.5	1.9
1105.5	0.69	0.66	0.43	0.082	2.41	42.0	5.4	1.6	1.5
1112.0	0.57	0.41	0.34	0.090	2.71	36.2	4.8	5.8	2.2
1118.5	0.67	0.54	0.31	0.040	2.12	35.4	-2.5	4.6	2.7
1127.0	4.35	0.87	0.91	0.468	12.95	67.7	8.7	23.0	3.2
1137.0	4.69	0.82	1.94	0.138	13.36	65.9	5.1	22.4	8.7
1147.0	4.16	0.84	1.26	0.000	12.38	65.8	3.0	20.3	7.7
1156.0	3.72	0.86	1.14	0.000	11.65	64.6	7.0	18.0	3.9
1161.0	2.29	0.33	0.99	0.000	10.23	60.6	-1.7	10.6	6.2
1171.0	3.08	0.36	1.49	0.036	11.45	64.8	1.1	14.5	9.4
1181.0	4.14	0.44	2.03	0.030	13.73	67.7	-0.6	21.2	17.2
1191.0	3.72	0.38	2.05	0.034	12.74	66.0	1.4	20.5	14.3
1201.0	2.78	0.34	1.26	0.154	11.57	63.1	-0.2	15.0	5.3
1211.0	2.64	0.38	1.44	0.056	11.66	63.9	1.5	14.9	6.7
1221.0	2.39	0.32	1.48	0.037	11.49	60.7	4.3	13.3	11.5
1236.0	3.19	0.31	1.21	0.000	11.55	62.5	1.2	13.7	17.3
1246.0	2.64	0.27	1.25	0.000	12.03	56.7	0.7	11.6	13.8
1255.0	3.07	0.28	1.21	0.000	11.60	58.4	-0.3	11.8	17.9
1264.0	3.01	0.29	1.29	0.000	11.46	58.6	1.5	16.1	20.7
1274.0	2.49	0.27	2.08	0.039	11.33	59.5	1.1	14.6	16.7
1281.0	1.59	0.19	1.16	0.000	9.84	46.4	-1.8	8.9	7.2

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1288.0  2.45  0.30  1.47  0.000  11.31  58.4   -0.6   14.2    8.7
1298.0  2.62  0.32  1.90  0.034  12.18  62.4    0.1   10.5    9.5
1308.0  2.35  0.32  1.77  0.024  12.46  60.6   -4.7   10.3    6.4
1320.0  2.08  0.26  1.18  0.000  11.55  51.7   -1.6   10.9    4.8
1327.0  2.26  0.32  1.49  0.027  10.48  63.6    0.2   10.5    9.7
1335.0  2.38  0.31  2.30  0.000  11.50  63.7   -1.7   12.3   12.0
1344.0  2.50  0.28  1.53  0.529  12.45  59.5   -0.8   10.2   12.0
1349.0  3.55  0.34  2.17  0.000  13.45  60.8   -5.3   23.8   17.2
1359.0  6.18  0.49  3.07  0.000  18.20  70.3   -5.2   37.1   24.1
1369.0  3.33  0.31  2.24  0.000  13.24  58.2   -3.0   18.3   20.5
1379.0  3.41  0.33  3.31  0.175  15.08  63.2   -0.4   16.9   30.9
1389.0  2.46  0.25  2.27  0.666  13.94  58.9  -10.6   13.2   17.6
1398.0  1.84  0.24  1.44  0.374  11.30  51.7    0.8   11.9   12.9
1410.0  1.34  0.22  2.11  0.073  10.78  50.9   -4.1    6.6   14.2
1420.0  1.07  0.20  1.56  0.053   9.82  41.6    2.0    5.3    4.3
1430.0  1.34  0.18  1.44  0.046   8.87  36.7   -3.3    6.6    3.7
1438.5  0.13  0.06  0.88  0.050   5.17  31.3   -7.9    8.8    6.2
1446.0  0.58  0.05  0.85  0.580   6.38  27.6   -8.9    7.9    6.7
1453.0  0.19  0.04  0.89  0.059   4.60  29.5   -4.4    6.8    5.7
1464.0  2.35  0.28  2.25  0.339  12.06  56.5   -6.6    9.2   33.3
1475.0  2.43  0.26  1.56  0.961  12.98  52.5   -0.5    4.0   14.6
1486.0  1.96  0.29  1.62  0.488  12.11  51.9   -0.5    5.7   12.2
1496.5  1.65  0.28  2.06  0.147  11.48  54.9   -5.3    4.5   10.8
1507.0  2.22  0.28  2.04  0.649  12.73  56.4   -1.4    5.8   11.0
1517.0  2.51  0.25  2.08  1.063  14.04  54.3   -4.6    5.4   12.3
1527.0  1.35  0.26  2.13  0.000  10.98  55.0   -7.3    5.0   10.4
1537.0  1.64  0.27  2.05  0.240  11.62  52.7   -3.5    4.7    9.9
1595.5  1.30  0.32  1.61  0.425  10.29  49.8   -3.5    5.3    9.1
1605.5  0.95  0.35  1.51  0.246   9.46  44.7   -1.5    4.0    8.8
1618.0  1.75  0.32  2.48  0.374  11.63  52.9    5.2    7.0   13.0
1627.0  1.75  0.21  1.52  0.102  11.66  43.8    4.4    5.1    8.8
1636.5  2.14  0.23  2.79  0.509  13.93  53.1   -2.7   10.4   14.8
1645.5  2.03  0.39  1.01  1.502   7.90  37.1   -3.1    4.3    5.8
1654.5  3.26  0.26  4.37  0.945  16.85  60.7    4.7   12.8   15.7
1664.5  3.67  0.23  2.41  1.176  15.58  56.5  -13.3   11.6    8.4
1674.5  0.74  0.42  0.28  0.486   3.95  24.0   -1.1    1.1    3.6
1685.0  3.94  0.24  3.59  1.722  18.92  62.3   -3.7   14.5   21.8
1695.0  2.96  0.20  1.78  0.801  14.61  51.8   -6.2    6.4    8.5
1704.0  5.46  0.18  3.60  3.238  21.45  59.7   -2.4   12.2   16.5
1727.0  2.37  0.22  1.24  0.964  11.78  43.3   -2.3    7.4    6.0
1746.0  2.47  0.22  5.57  0.107  18.33  63.5    6.2   12.2   39.8
1756.5  2.90  0.38  3.95  0.105  14.08  58.3    2.6    7.5   27.8
1765.5  4.20  0.27  5.15  1.585  18.26  59.3   -6.5    7.7   28.1
1774.5  4.68  0.31  3.15  2.392  17.60  52.4   -1.2    8.9   15.2
1783.5  5.31  0.27  6.57  2.361  20.63  58.1  -14.2   10.7   29.6
1794.0  4.99  0.31  4.28  2.133  18.85  58.2  -10.7   11.2   19.8
1804.5  5.01  0.27  3.91  2.130  18.83  56.5  -11.2    8.7   25.1
1821.5  3.92  0.27  2.61  1.584  15.80  55.6   -8.5   12.3   34.5
1832.0  2.51  0.31  3.88  0.089  14.02  54.6    1.9   10.2   25.9
1842.0  2.43  0.25  2.33  0.440  12.42  46.8   -3.9    5.6   13.2
1851.0  2.72  0.29  2.39  0.641  13.26  47.8    1.8    3.5   10.9
1860.0  4.43  0.19  1.40  2.988  16.51  45.8   -3.6    3.5   11.4
1869.0  5.02  0.21  1.09  3.518  18.78  44.8  -11.4    1.3   10.0
1878.5  3.11  0.16  1.12  2.126  14.49  38.2    2.0    1.0   12.0
1888.0  3.88  0.21  0.94  2.637  16.45  35.3   -2.3   -0.9   11.4
1898.0  3.39  0.17  1.00  2.251  15.92  34.3   -9.2   -1.0   13.4
1909.0  2.30  0.16  1.07  1.577  13.13  31.8   -2.6   -2.7   10.4
1929.0  2.14  0.22  0.89  1.135  10.85  33.1   -6.8   -0.3    8.6
1940.5  2.53  0.15  0.92  1.755  13.53  34.5  -16.4   -3.5   12.7
1949.5  1.34  0.20  0.96  0.601  10.06  34.0    1.6   -2.3   10.2
1959.0  1.51  0.15  1.00  0.902  10.27  33.4   -7.2   -3.6   12.2
1969.0  1.56  0.14  0.93  0.755  10.65  35.2    4.6    0.2   11.0
1979.0  1.71  0.18  0.93  1.003  10.74  32.0   -6.0   -2.8    8.6
1988.0  1.63  0.16  0.85  1.073  10.25  31.7   -5.5   -1.9   10.2
1997.5  1.60  0.16  1.07  0.886  10.77  33.9    0.4   -2.0   12.2
2006.5  1.47  0.14  1.02  0.790  10.40  33.8    4.8   -3.5   13.2
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2015.5  1.02  0.14  1.02  0.477   8.51  32.3    2.7   -3.5   17.6
2026.0  1.19  0.13  1.34  0.527   8.92  33.3    0.6   -4.3   11.1
2035.0  1.42  0.13  1.31  0.603   9.51  33.2   -1.3   -2.3   14.3
2044.0  1.32  0.14  1.37  0.682   9.30  33.8    8.5   -5.6   11.8
2053.5  1.22  0.12  1.22  0.652   8.82  32.2   -1.3   -3.4   10.4
2064.0  1.45  0.11  1.28  0.896   9.97  35.2   -2.4   -3.4   16.8
2080.0  1.49  0.09  1.30  0.907   9.81  35.4    2.2   -3.4   14.2
2096.0  1.33  0.10  1.24  0.846   9.16  34.4   -0.6   -1.6   21.2
2114.0  1.32  0.15  1.28  0.829   9.87  37.5   -2.1   -2.7    7.5
2239.5  1.33  0.09  1.27  0.953   6.94  25.1   -0.2   -0.5   10.4
2248.5  3.55  0.24  1.40  1.716  14.50  50.8   -0.8    6.3    8.3
2258.0  1.95  0.17  1.73  0.329  10.58  59.9   -2.1    7.8   12.8
2267.0  1.58  0.14  1.44  0.225   9.56  56.0   -0.8    7.8   11.8
2276.0  2.01  0.16  1.61  0.337  10.82  55.9   -6.9    9.5   10.9
2285.5  2.72  0.16  1.33  0.842  12.77  59.7   -9.4    9.5   10.4
2294.5  2.62  0.14  1.75  1.064  12.92  58.1   -8.5    7.9   11.5
2303.5  2.04  0.10  1.38  1.197  11.05  43.3  -15.5    4.5    8.5
2313.0  1.63  0.16  1.79  0.202  10.56  57.6   -3.0    9.1    9.5
2349.5  0.73  0.14  1.45  0.000   9.02  47.2   -1.3    4.0    6.1
2360.0  1.29  0.14  1.55  0.312  10.38  49.5   -2.7    4.0    5.3
2370.0  2.33  0.15  1.94  0.364  11.16  51.4    0.4   19.4    8.0
2379.0  1.49  0.15  2.13  0.199  10.61  52.7    0.6    8.1    5.0
2389.0  1.27  0.16  2.14  0.187  10.96  51.9   -3.0    3.8    4.1
2399.0  0.86  0.14  2.12  0.086  10.03  50.6   -0.8    2.9    5.0
2413.5  0.84  0.14  1.91  0.264  10.31  45.6   -1.1    3.5    5.7
2423.0  0.89  0.11  1.88  0.286  10.00  43.7   -2.9    3.5    4.1
2432.5  0.81  0.10  1.94  0.146  10.04  39.1   -6.2    1.5    4.0
2445.5  1.15  0.12  1.66  0.000   8.80  36.2   -4.7    4.8    3.4
2457.5  0.69  0.09  1.43  0.000   7.11  34.3   -8.0    5.1    4.6
2470.0  0.00  0.05  0.99  0.000   3.70  46.1  -11.9    5.4    5.6
2480.0  0.53  0.08  1.56  0.038   8.16  40.8   -1.7    4.4    6.7
2490.0  1.08  0.15  1.60  0.076   8.62  40.3    7.6    6.8    4.9
2499.5  1.40  0.20  1.99  0.000   9.48  51.7   -8.3    7.0    4.8
2508.5  1.83  0.19     *  0.436  10.19  56.8  -11.6    6.1    5.2
2518.0  1.96  0.19     *  0.368  10.74  55.2   -7.1    6.3    6.4
2527.0  1.80  0.21     *  0.079  10.43  55.9   -6.3    8.3    4.9
2549.5  1.75  0.19     *  0.082  10.27  59.7   -5.0    7.2    5.7
2561.0  1.77  0.21     *  0.457  10.39  53.6   -4.9    4.4    6.4
2570.0  3.91  0.17     *  2.130  16.66  56.4  -15.4    8.3   11.4
2579.0  1.48  0.23     *  0.063  10.42  58.8    0.6    6.4   12.4
2588.0  1.75  0.20     *  0.199  11.20  54.6    2.0    6.9    6.8
2609.5  1.32  0.20     *  0.500  11.40  48.5   -4.9    0.1    3.8
2620.0  1.75  0.17     *  0.724  11.82  46.9   -3.5    2.9    5.9
2631.5  1.07  0.18     *  0.066   9.13  44.4   -5.2    4.8    7.5
2645.0  1.91  0.23     *  0.000  10.78  58.9    1.4   10.8    7.3
2654.0  1.16  0.21     *  0.000   9.18  53.2   -3.7    4.5    4.6
2663.5  1.69  0.23     *  0.000   9.06  58.8    3.2   10.5    6.1
2672.5  3.80  0.19     *  2.436  15.88  55.9   -1.4    9.7    5.8
2681.5  2.25  0.25     *  0.100  10.84  62.9   -2.5   10.6    9.3
2690.5  2.55  0.27     *  0.171  11.47  61.3   -1.2   14.5   11.3
2699.5  3.32  0.27     *  0.829  13.19  62.3    5.5   12.6    9.2
2708.0  3.12  0.23     *  1.155  12.95  58.7   -9.7   10.3   11.9
2717.5  3.12  0.29     *  0.573  12.63  63.5   -4.7   18.2   13.3
2729.0  3.23  0.34     *  0.051  12.56  62.2   -5.7   23.4   16.9
2748.0  3.22  0.36     *  0.000  12.56  62.0   -7.1   26.6   15.5
2826.5  3.06  0.31     *  0.239  12.36  58.0   -3.3   21.1   10.8
2855.5  2.06  0.27     *  0.000   9.97  55.2   -2.8   19.8   15.7
2874.0  2.42  0.30     *  0.000  10.26  57.9   -3.8   12.9   10.6
2883.0  4.38  0.25     *  2.089  15.99  57.1   -3.6   10.5   10.0
2892.5  2.79  0.31     *  0.000  11.87  59.9   -1.2   13.1   12.7
2902.0  2.41  0.29     *  0.000  11.25  56.6    2.7   13.6    9.7
2911.0  2.41  0.30     *  0.000  11.01  56.5    4.6   12.4    8.8
2920.5  2.17  0.28     *  0.000  11.48  47.8    2.5    9.6    5.8
2930.5  2.29  0.28     *  0.032  11.80  52.6   -6.9   12.8    8.3
2952.5  2.06  0.29     *  0.000  11.63  48.3    3.2    6.7    3.6
2964.0  2.27  0.30     *  0.000  11.12  55.7   -2.4   11.3    4.3
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2976.5   2.36   0.30      *  0.000  11.08  58.8    6.0   12.8    7.2
2989.5   2.67   0.29      *  0.151  12.12  62.4    4.0   13.2    6.2
3000.0   2.87   0.27      *  0.309  12.22  61.2   -2.5   11.7    7.4
3011.5   2.82   0.28      *  0.000  12.02  60.9    8.1   13.2    8.9
3021.5   2.81   0.27      *  0.062  11.61  61.7    1.0   14.1    9.0
3031.5   2.84   0.24      *  0.115  11.37  62.4   -5.2   13.0    7.7
3044.5   2.95   0.25      *  0.376  11.74  61.8   -1.7   12.6   10.3
3056.0   3.81   0.20      *  1.617  13.65  56.7    0.4   10.8    6.7
3067.5   4.03   0.22      *  1.563  15.27  60.0    8.6   13.3    7.2
3078.0   2.56   0.28      *  0.000  12.94  62.0    5.4   16.9    7.5
3088.0   2.47   0.24      *  0.322  12.97  57.4   -1.2   13.6    6.5
3098.5   2.44   0.23      *  0.399  12.79  53.5   -1.6   14.3    4.8
3110.0   1.91   0.20      *  0.000  11.48  51.8    2.8   12.6    6.8
3122.0   1.90   0.17      *  0.000  11.72  50.5    5.6   11.3    7.1
3155.5   1.99   0.18      *  0.000  11.57  55.8   -4.2   10.5    4.5
3166.0   1.92   0.20      *  0.000  10.88  56.8    1.1   12.5    8.2
3176.5   2.22   0.17      *  0.000  12.74  59.9    1.6   14.0    7.1
3187.0   2.88   0.20      *  0.299  13.50  61.1    6.9   12.3    6.8
3197.0   3.32   0.20      *  0.970  14.93  59.5    6.7   12.4    7.0
3207.0   2.13   0.16      *  0.000  11.75  60.7    1.5   13.5   14.9
3217.5   2.22   0.19      *  0.000  12.16  56.5   -1.9   13.5    9.6
3226.5   2.20   0.20      *  0.000  12.64  56.5    3.8   11.2   10.2
3236.5   2.50   0.20      *  0.000  11.98  57.1    1.3   10.3   14.0
3249.5   2.28   0.15      *  0.000  12.94  63.0    5.9   12.8   12.1
3258.5   2.79   0.20      *  0.137  12.84  56.5   -1.1   11.5   10.8
3268.0   2.64   0.17      *  0.000  12.31  59.0   10.5   11.8   17.3
3277.0   2.51   0.16      *  0.000  12.11  58.7   -2.0   13.3   13.0
3286.5   2.44   0.16      *  0.000  10.89  60.1    0.5   13.1   11.8
3297.5   2.43   0.27      *  0.000  11.22  57.1    1.2   11.9   11.3
3307.5   3.06   0.24      *  0.000  13.00  63.0   -1.3   14.4   15.4
3317.0   2.93   0.18      *  0.000  12.97  64.1    3.8   16.1   20.4
3326.0   3.14   0.23      *  0.000  12.48  63.9    1.1   20.3   11.6
3337.0   2.86   0.20      *  0.000  12.53  63.6    0.4   17.3   13.9
3356.5   2.91   0.18      *  0.000  12.29  62.5    3.1   16.1   18.1
3367.0   3.00   0.19      *  0.000  12.37  62.6   -3.6   17.4   19.5
3378.5   3.19   0.27      *  0.051  13.27  61.6   -4.9   17.9   11.7
3390.0   2.48   0.14      *  0.000  12.96  62.4   -1.4   20.5   26.0
3402.5   3.13   0.23      *  0.000  12.63  63.8  -11.5   19.9   27.9
3412.0   4.02   0.27      *  0.000  14.11  65.3   -5.5   26.6   20.3
3422.5   3.45   0.24      *  0.000  13.78  64.6    3.0   22.4   20.8
3433.5   3.20   0.23      *  0.000  13.32  63.3   -2.4   22.5   19.0
3444.0   2.27   0.15      *  0.000  12.00  59.0   -0.5   19.2   21.3
3454.0   2.03   0.17      *  0.000  12.04  54.3    3.1   14.5   14.7
3464.0   2.46   0.18      *  0.254  13.44  56.2    4.2   15.7   16.4
3474.5   2.62   0.17      *  0.000  13.33  55.6   -0.8   19.2   19.1
3485.0   2.22   0.19      *  0.000  12.88  53.1   -4.3   22.6   11.7
3495.5   2.75   0.30      *  0.000  12.12  58.3    4.7   19.7   12.3
3504.5   2.97   0.30      *  0.044  12.66  56.9   -1.0   17.9    8.8
3514.5   2.62   0.28      *  0.044  12.10  55.9    0.8   15.0    9.7
3524.5   1.62   0.23      *  0.166  10.76  48.5   -2.1   11.6    8.4
3534.0   2.34   0.30      *  0.294  12.81  52.9    1.2   11.5    7.2
3543.0   2.38   0.28      *  0.000  12.30  54.4    7.5   14.7    9.4
3561.0   2.98   0.30      *  0.000  13.17  59.5    6.8   18.5   16.3
3571.5   2.69   0.30      *  0.000  12.62  60.2    6.0   13.8   14.2
3581.5   2.75   0.28      *  0.000  12.32  63.8    3.3   20.2   20.4
3591.0   1.57   0.32      *  0.000  10.84  55.9   -6.3    8.7   13.6
3600.0   1.47   0.27      *  0.056  10.07  51.8   -8.2   11.3    8.9
3609.0   2.01   0.25      *  0.176  11.60  54.4    2.9   16.9    9.3
3619.5   1.96   0.25      *  0.274  11.47  51.7   -1.3   10.6    9.6
3630.0   2.13   0.24      *  0.199  11.82  52.1    0.2   10.9    8.1
3642.0   2.52   0.25      *  0.231  12.36  54.6    2.3   13.5   10.5
3666.0   1.50   0.28      *  0.056  11.63  48.8    9.2   10.2   10.2
3677.5   1.49   0.23      *  0.255  11.84  49.1   -9.3    9.7   13.0
3705.5   1.21   0.22      *  0.000  10.34  50.5   -4.7    7.7   10.7
3717.0   2.01   0.27      *  0.038  11.08  53.9   -3.4   12.7    6.0
3727.5   1.51   0.24      *  0.097   9.66  44.9   -3.6    5.9    7.0
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3738.0   2.04   0.27      *  0.000  11.57  51.0   -0.2    9.6   16.1
3768.0   1.21   0.22      *  0.029   9.63  44.9   -1.1    4.1   11.5
3779.5   1.19   0.22      *  0.000   8.89  44.5   -2.9    7.6    7.2
3790.0   1.57   0.25      *  0.000  10.41  50.9   -9.7    7.6   13.0
3800.0   1.73   0.25      *  0.000  11.28  51.0   -1.7    8.1   15.5
3810.5   1.96   0.27      *  0.000  11.71  51.3    1.6    9.9   16.1
3854.0   2.07   0.29      *  0.086  11.75  57.5    0.3    9.2   17.4
3864.0   1.12   0.27      *  0.056   9.84  42.2    6.3    3.3    7.0
3876.0   1.47   0.25      *  0.138  10.50  44.1   -3.1    6.3    7.8
3886.0   1.54   0.26      *  0.119  10.70  49.6   -2.8    8.7   10.7
3896.5   1.07   0.37      *  0.042   9.34  40.1   -1.2    2.6    5.2
3908.5   1.30   0.24      *  0.135  10.54  43.5    4.7    3.9    6.6
3919.5   1.28   0.27      *  0.141  10.50  43.3   -3.1    5.4   10.3
3938.5   1.32   0.21      *  0.332  10.30  41.3    0.8    2.5    6.8
3948.0   1.44   0.25      *  0.099  11.32  48.2   -1.1    5.6   11.2
3957.0   1.03   0.19      *  0.050  10.38  43.5    3.3    4.4    7.9
3967.0   1.36   0.23      *  0.063  11.04  48.1    5.2    5.0   10.8
3977.5   1.32   0.21      *  0.191  11.13  45.3   -4.6    3.6    8.4
3988.0   1.44   0.17      *  0.679  11.86  40.4   -5.2   -1.0    6.4
3998.0   1.48   0.16      *  0.761  12.11  40.0    2.6    0.7    5.1
4008.5   0.87   0.18      *  0.101  10.35  38.4    4.7    1.4    3.8
4017.5   1.28   0.23      *  0.000  11.13  42.1   -1.3    5.3    5.1
4029.0   1.03   0.19      *  0.217  10.42  38.4    3.8    1.7    6.2
4052.0   1.44   0.22      *  0.274  10.97  46.1   -5.8    5.0    7.0
4062.5   2.21   0.21      *  0.993  12.76  42.9    1.9    5.8    8.5
4073.0   1.39   0.24      *  0.216   9.66  42.9    8.9    5.3    6.3
4083.5   1.26   0.25      *  0.000   9.68  42.4   -2.4    5.9    5.5
4097.0   1.40   0.23      *  0.278  11.32  40.8   -2.9    5.1    7.2
4106.5   1.81   0.25      *  0.359  12.62  44.9   -4.8    5.3   10.0
4120.0   1.72   0.25      *  0.069  10.72  43.4   -2.3   14.1    5.5
4130.5   1.63   0.25      *  0.056  10.73  44.5   -2.7    8.3    6.3
4139.5   1.79   0.25      *  0.178  11.46  46.2    0.5   10.6    4.8
4149.0   2.61   0.22      *  0.985  13.22  45.1    2.6   15.3    4.3
4158.0   1.30   0.25      *  0.065  10.46  41.1    1.1    4.4    3.9
4167.5   1.38   0.24      *  0.000  10.56  42.2    7.0    6.0    4.9
4176.5   1.24   0.22      *  0.000  10.28  39.5   -7.0    5.2    4.4
4185.5   2.50   0.21      *  1.309  13.49  35.6   -2.0    5.6    4.8
4210.0   1.31   0.24      *  0.065   9.89  39.2    6.5    6.1    4.5
4220.5   1.40   0.33      *  0.045   9.40  43.5   -3.5    8.8    3.5
4231.0   3.90   0.20      *  2.295  16.07  47.9   -5.0   15.9    5.2
4241.0   2.06   0.23      *  0.486  11.12  46.9    6.1   11.8    6.9
4251.5   1.00   0.17      *  0.000   8.23  38.5   -6.7    1.8    4.5
4262.0   1.73   0.25      *  0.063  10.64  45.7    0.0    9.6    6.5
4272.5   2.05   0.25      *  0.341  10.92  48.6   -8.2   11.5    4.4
4281.5   1.51   0.20      *  0.342  10.93  38.2   -6.2    6.5    5.7
4290.5   1.76   0.26      *  0.031  10.83  45.1   -5.5    8.3    7.7
4303.5   1.42   0.20      *  0.224   9.93  38.3   -6.0    5.2    5.7
4312.5   1.58   0.21      *  0.131  10.71  44.0   -1.4   10.6    4.5
4323.0   1.32   0.23      *  0.031  10.32  40.0   -1.1    7.7    5.2
4333.0   1.56   0.27      *  0.026  10.55  42.3   -4.7   11.7    6.4
4342.0   1.87   0.26      *  0.086  10.61  46.1   -3.3   16.0    6.7
4351.0   3.28   0.18      *  2.111  14.51  37.4   -7.6   10.9    5.7
4361.0   1.57   0.26      *  0.000   9.88  43.6    7.5    9.3    5.1
4371.0   1.74   0.28      *  0.035  10.72  46.3    0.4    8.7    6.5
4380.0   2.10   0.27      *  0.000  11.01  51.4   -9.6   13.2    9.7
4390.0   2.28   0.29      *  0.000  11.41  51.6   -0.4   13.2    8.5
4412.0   1.88   0.27      *  0.000  11.38  46.6   -3.6    5.5    8.0
4421.0   2.25   0.30      *  0.069  11.40  51.0    5.1   13.4    9.6
4437.5   1.56   0.26      *  0.000  10.78  46.4   -9.9    5.3   10.7
4446.5   1.91   0.28      *  0.034  10.96  46.6    0.5    6.9    9.8
4456.0   1.63   0.27      *  0.082   9.74  45.6    5.3    9.9    8.1
4465.0   2.35   0.31      *  0.174  11.30  52.2   -5.4   11.9    8.6
4473.5   2.26   0.31      *  0.111  11.33  50.2   -2.7   10.1    9.5
4486.0   1.79   0.25      *  0.040  10.02  42.8    0.3    6.4    5.8
4496.0   2.41   0.28      *  0.064  11.21  50.0   -1.4   15.2    6.5
4509.5   2.34   0.30      *  0.000  11.49  50.2   -2.6   13.1    8.6
```

```
4519.0   2.50   0.27     * 0.028  11.69  49.6    2.1   19.7    6.7
4528.0   3.03   0.25     * 0.709  13.08  46.2   -4.0   18.3    7.2
4548.0   1.68   0.21     * 0.000   9.22  38.4  -11.1    7.9    8.8
4556.0   2.37   0.26     * 0.081  11.61  43.4  -15.8    8.4    6.6
4564.0   2.17   0.31     * 0.076  11.07  45.3   -6.5   10.2    6.2
4577.0   1.39   0.20     * 0.083   8.48  32.9  -12.9    5.8    4.3
4588.0   2.13   0.28     * 0.476  10.72  41.5   -0.6   10.1    7.2
4597.5   2.42   0.26     * 0.669  11.92  38.8   -1.2    9.0    6.6
4607.0   1.62   0.25     * 0.022  10.31  39.8   -8.1    5.7    4.6
4618.0   1.97   0.26     * 0.000  10.71  44.9   -2.3    8.3    5.9
4630.5   2.25   0.25     * 0.050  10.51  49.7   -5.2   13.4    7.6
4641.0   2.21   0.28     * 0.000  10.70  48.3   -6.3   10.5    9.0
4651.0   2.75   0.27     * 0.168  11.90  51.4    7.7   16.0    7.7
4661.0   2.41   0.20     * 0.501  10.36  40.7   -2.8   12.4    5.3
4671.5   2.93   0.27     * 0.000  11.49  52.9    1.1   13.4    7.4
4681.5   2.20   0.28     * 0.000  11.00  49.1   -0.9   12.8    6.3
4691.5   1.62   0.14     * 0.089   9.37  31.5   -2.3    5.4    4.7
4710.0   2.70   0.29     * 0.000  11.43  45.8    0.0   11.1    5.8
4718.5   2.31   0.31     * 0.000  10.85  54.9   -5.1   11.9    6.5
4730.0   2.13   0.30     * 0.000  10.79  50.4    3.9   11.1    8.9
4740.0   2.19   0.31     * 0.061  11.40  50.7    4.2   12.1    6.2
4751.5   1.99   0.25     * 0.055   9.83  49.0    3.0   15.4    7.8
4763.0   1.79   0.23     * 0.000   9.09  49.1   -6.9   11.2    7.8
4773.0   2.38   0.24     * 0.000  11.63  46.8   -0.3   10.8    8.3
4822.5   1.29   0.21     * 0.055  10.35  38.6   -0.5    4.9    6.6
4839.0   1.51   0.19     * 0.000   9.43  36.0   -2.4    3.5    3.1
4849.5   1.68   0.22     * 0.000  10.64  42.3   -4.5    6.4    2.3
4859.5   2.59   0.33     * 0.000  11.81  47.2    5.4    8.9    5.5
4870.0   3.10   0.30     * 0.000  12.13  54.8    1.2   13.1    9.9
4880.0   3.14   0.35     * 0.000  12.83  54.5   -4.7   13.0   10.8
4893.0   3.54   0.29     * 0.000  13.19  54.7   -7.0   18.5   17.5
4902.5   4.58   0.30     * 0.536  15.01  59.4    2.4   21.1   10.6
4913.0   3.74   0.31     * 0.218  13.27  55.9    0.2   15.2   18.0
4923.5   3.77   0.27     * 0.131  12.87  58.1   -0.2   15.2   19.6
4933.0   4.12   0.27     * 0.773  14.60  55.4   -3.6   15.3   12.8
4943.0   3.24   0.31     * 0.045  12.96  52.5   -4.1   16.3   15.1
4953.5   3.20   0.28     * 0.030  12.94  52.8    3.8   20.7   14.4
4962.5   3.93   0.19     * 1.472  15.86  46.5   -4.9   19.2    6.3
4971.5   2.95   0.22     * 0.043  13.17  45.5    3.5   21.6    5.3
5006.5   2.47   0.25     * 0.075  12.10  48.9   -9.0   15.3    6.7
5015.5   2.47   0.16     * 0.573  11.75  41.0   -9.9   10.9    5.0
5025.0   2.22   0.30     * 0.039  11.89  45.7    2.3   14.7    5.1
5034.0   1.97   0.26     * 0.299  11.90  44.4   -4.8    7.7    5.8
5043.0   1.70   0.19     * 0.348  11.46  37.4   -3.2    6.5    4.9
5052.0   1.50   0.17     * 0.241  11.29  36.5   -3.8    3.8    5.1
5061.0   1.04   0.17     * 0.217   9.58  31.8  -15.5    4.3    5.4
5070.0   1.53   0.12     * 0.127  11.53  31.6   -6.5    2.6    3.5
5079.0   2.44   0.24     * 0.052  11.93  34.7    4.2    6.2    4.6
5089.0   3.07   0.15     * 1.212  14.18  41.2   -1.8    4.8    5.6
```

depth	del C-13	depth	Bsilica	depth	HI
5.0	-22.594	5.0	16.06	5.0	292.0
15.0	-22.952	15.0	30.14	15.0	324.8
95.0	-24.614	25.0	29.09	55.0	291.0
183.0	-24.556	35.0	33.52	65.0	286.7
223.0	-25.044	45.0	40.81	95.0	272.0
283.0	-25.111	55.0	56.22	115.0	276.4
362.5	-23.441	65.0	63.46	155.0	326.1
417.0	-23.833	75.0	53.42	183.0	408.0
457.0	-23.197	85.0	50.82	193.0	436.1
517.0	-24.444	95.0	52.60	223.0	426.4
555.0	-24.607	105.0	41.80	283.0	533.3
562.0	-24.624	115.0	6.80	320.5	153.1
577.0	-24.712	125.0	49.51	362.5	337.7
597.0	-25.567	135.0	60.85	417.0	325.8
634.0	-24.439	145.0	59.26	457.0	380.6
667.0	-24.187	155.0	57.71	517.0	329.9
677.0	-22.464	165.0	53.20	537.0	325.2
687.0	-22.155	183.0	53.95	562.0	342.6
697.0	-23.812	193.0	50.63	597.0	444.2
707.0	-23.718	203.0	56.76	634.0	327.3
717.0	-24.018	213.0	61.24	657.5	379.4
727.0	-24.288	223.0	48.99	667.0	422.7
737.0	-23.839	233.0	44.20	677.0	342.6
747.0	-24.224	243.0	41.30	687.0	363.0
756.5	-25.237	253.0	47.86	697.0	393.0
776.5	-25.056	263.0	39.95	707.0	365.2
785.0	-25.345	273.0	41.86	717.0	384.2
794.0	-24.990	283.0	45.18	727.0	289.0
804.0	-24.375	293.0	51.26	737.0	310.9
814.5	-24.969	303.0	53.88	747.0	300.4
825.0	-24.217	310.5	27.94	756.5	285.5
835.0	-23.839	315.5	0.87	776.5	313.8
845.0	-23.950	320.5	1.39	785.0	142.1
855.0	-23.481	327.5	45.33	794.0	267.1
865.0	-23.934	335.5	0.04	804.0	298.8
877.0	-23.498	343.0	35.67	814.5	312.6
887.0	-23.188	353.0	31.96	825.0	294.2
897.0	-24.156	362.5	29.91	835.0	249.8
906.0	-24.049	377.0	18.19	845.0	294.8
915.0	-23.862	387.0	27.68	855.0	311.1
924.5	-23.987	397.0	39.02	865.0	297.6
932.5	-22.899	407.0	32.44	877.0	279.5
941.0	-22.725	417.0	26.29	887.0	276.3
951.0	-22.079	427.0	24.25	897.0	314.5
961.0	-22.788	437.0	46.11	906.0	294.6
977.0	-22.971	447.0	33.47	915.0	270.5
987.0	-23.295	457.0	25.96	924.5	327.9
1057.0	-23.966	467.0	26.43	932.5	282.4
1137.0	-23.830	477.0	23.05	941.0	280.6
1181.0	-23.637	487.0	35.31	951.0	236.5
1236.0	-24.187	497.0	31.11	987.0	327.6
1298.0	-25.080	507.0	15.02	1057.0	296.2
1359.0	-25.430	517.0	31.85	1097.0	148.3
1398.0	-22.393	527.0	52.11	1112.0	68.7
1464.0	-25.463	537.0	63.43	1118.5	31.7
1537.0	-24.000	547.0	51.43	1137.0	324.5
1605.5	-24.276	555.0	46.57	1181.0	348.9
1695.0	-24.153	562.0	36.41	1236.0	316.3
1794.0	-24.238	577.0	28.40	1298.0	238.6
1832.0	-24.091	587.0	34.33	1344.0	210.0
1898.0	-24.000	597.0	34.23	1359.0	324.4
2044.0	-24.373	607.0	30.46	1398.0	183.5
2239.5	-23.953	617.0	27.71	1464.0	210.3
2258.0	-22.871	626.0	7.39	1537.0	145.7
2285.5	-22.275	634.0	30.60	1605.5	160.5

2349.5	-23.892	642.0	13.86	1695.0	124.1
2423.0	-25.089	649.5	3.47	1704.0	237.6
2561.0	-24.503	657.5	10.37	1756.5	108.4
2663.5	-22.756	667.0	28.89	1783.5	189.2
2883.0	-23.735	677.0	18.43	1794.0	172.6
2920.5	-24.932	687.0	30.64	1804.5	171.2
3044.5	-24.524	697.0	32.00	1832.0	85.5
3056.0	-24.156	707.0	32.85	1851.0	78.4
3122.0	-24.971	717.0	42.67	1878.5	92.5
3207.0	-25.351	727.0	47.60	1940.5	64.5
3226.5	-25.742	737.0	49.83	1997.5	68.6
3268.0	-26.840	747.0	41.85	2044.0	48.6
3307.5	-26.173	756.5	41.23	2114.0	67.2
3317.0	-26.979	776.5	29.16	2239.5	61.0
3326.0	-26.173	785.0	6.19	2258.0	211.6
3337.0	-25.653	794.0	43.70	2285.5	226.3
3356.5	-25.700	804.0	34.47	2423.0	155.6
3367.0	-24.658	814.5	25.92	2432.5	114.5
3378.5	-24.194	825.0	25.49	2445.5	111.3
3390.0	-24.647	835.0	32.76	2527.0	148.2
3402.5	-25.436	845.0	45.18	2561.0	166.0
3412.0	-23.699	855.0	46.41	2588.0	143.8
3422.5	-24.099	865.0	21.19	2681.5	186.5
3433.5	-23.723	877.0	33.35	2717.5	209.7
3444.0	-23.902	887.0	31.49	2729.0	183.1
3454.0	-23.125	897.0	33.78	2883.0	247.1
3485.0	-21.887	906.0	21.82	2920.5	141.9
3591.0	-21.660	915.0	33.67	2952.5	134.5
3768.0	-23.071	924.5	26.63	3011.5	189.4
4017.5	-21.066	932.5	19.09	3044.5	218.3
4185.5	-24.415	941.0	35.54	3056.0	233.0
4380.0	-23.405	951.0	28.24	3122.0	219.5
4548.0	-23.322	961.0	31.17	3166.0	222.9
4671.5	-24.045	1087.0	25.02	3207.0	262.9
4822.5	-22.298	1097.0	5.44	3226.5	233.2
4859.5	-24.901	1288.0	21.88	3268.0	281.1
4893.0	-24.126	1298.0	22.07	3307.5	329.1
4902.5	-23.619	1389.0	13.87	3317.0	309.9
4913.0	-23.825	1464.0	17.54	3326.0	279.6
4923.5	-24.080	1595.5	12.20	3356.5	280.1
4933.0	-24.206	1685.0	15.34	3378.5	224.0
4953.5	-23.516	1765.5	16.95	3402.5	192.0
5015.5	-23.194	1774.5	10.98	3412.0	260.4
5052.0	-25.093	1794.0	20.52	3422.5	258.6
5089.0	-24.523	1804.5	20.01	3433.5	259.4
*	*	1821.5	13.79	3444.0	229.5
*	*	1959.0	-0.58	3454.0	168.0
*	*	1969.0	-0.58	3464.0	223.5
*	*	1997.5	-1.17	3474.5	196.9
*	*	2006.5	-0.98	3485.0	227.0
*	*	2096.0	-0.85	3495.5	198.5
*	*	2114.0	-0.71	3543.0	169.7
*	*	2285.5	44.13	3600.0	201.6
*	*	2294.5	54.25	3666.0	197.4
*	*	2303.5	12.21	3768.0	145.6
*	*	2445.5	-0.09	3864.0	122.2
*	*	2457.5	0.92	3919.5	118.5
*	*	2729.0	37.23	3998.0	94.6
*	*	2930.5	22.47	4052.0	139.8
*	*	2976.5	36.23	4130.5	165.8
*	*	2989.5	39.34	4185.5	143.6
*	*	3031.5	51.97	4281.5	112.2
*	*	3044.5	53.18	4342.0	164.8
*	*	3110.0	20.85	4412.0	148.9
*	*	3307.5	45.79	4473.5	170.3
*	*	3317.0	52.95	4548.0	116.1

```
    *         *          3326.0  42.02           4661.0  136.2
    *         *          3337.0  51.82           4730.0  160.1
    *         *          3356.5  61.18           4822.5   93.9
    *         *          3367.0  58.93           4859.5  126.6
    *         *          3378.5  46.79           4893.0  163.0
    *         *          3390.0  54.29           4902.5  235.9
    *         *          3402.5  59.07           4913.0  234.8
    *         *          3495.5  28.58           4923.5  266.0
    *         *          3504.5  20.55           4933.0  263.8
    *         *          3988.0   3.10           4953.5  187.1
    *         *          3998.0   2.64           5006.5  190.0
    *         *          4008.5   2.03           5015.5  145.0
    *         *          4017.5   6.82           5052.0  102.5
    *         *          4473.5  18.96           5061.0   79.0
    *         *          4486.0  12.56           5089.0  132.9
    *         *          4870.0  36.38                *      *
    *         *          4880.0  34.74                *      *
    *         *          4893.0  36.06                *      *
    *         *          4902.5  37.24                *      *
    *         *          4913.0  41.76                *      *
    *         *          4923.5  55.40                *      *
    *         *          4933.0  42.10                *      *
    *         *          4943.0  29.94                *      *
    *         *          5052.0   2.90                *      *
    *         *          5061.0   0.30                *      *
    *         *          5070.0   1.09                *      *
    *         *          5079.0   5.14                *      *
```

Palynofacies counts

The samples (A-H) are related to depth as follows:

A=185cm B=450cm BC=790cm C=1230cm D=1765
E=2000cm F=2495cm G=2754cm G1=3402cm H=3987cm

Sam	amo	gel	pin	pol	cut	lwd	dwd	spo	ped	bot	fun	chi	cla	zoo	amd	Tot
A	135	7	0	17	38	5	2	11	1	0	12	1	6	36	20	291
B	131	28	10	25	44	7	19	13	0	0	14	0	1	23	36	351
BC	92	2	1	17	20	3	8	3	7	1	8	2	2	40	16	222
C	192	14	9	29	52	1	6	3	2	9	11	2	3	77	97	507
D	189	5	7	32	16	1	5	3	0	5	6	3	3	31	18	324
E	114	1	2	1	7	0	5	1	0	0	2	0	0	2	7	142
F	158	6	1	13	13	0	4	3	0	3	9	0	1	5	30	246
G	142	1	5	16	25	0	3	4	1	1	9	1	0	11	19	238
G1	172	3	12	23	52	1	16	4	2	2	12	7	6	25	14	351
H	177	8	0	13	13	0	3	1	0	0	6	1	1	8	9	240

amo=amorphous organic matter
gel=gel-like organic matter
pin=conifer pollen
pol=other pollen types
cut=cuticle and plant tissue
lwd=pale woody material
dwd=dark woody material or charcoal
spo=spores

ped=Pediastrum
bot=Botryococcus
fun=fungal hyphae
chi=chironomids
cla=Cladocera
zoo=zooclasts (e.g. insect remains)
amd=amorphous degraded matter
Tot=total number of points counted

N-alkane concentrations

The n-alkane concentrations (nC_{17} to nC_{34}) are shown below (in µg alkane/g dry sediment) for the 10 samples analysed:

nC	183cm	457cm	785cm	877cm	951cm	1236cm	1794cm	2445cm	3317cm	3412cm
17	0.89	0.00	0.16	0.20	0.23	0.20	0.25	0.13	0.35	0.20
18	0.00	0.21	0.05	0.17	0.04	0.03	0.03	0.00	0.04	0.02
19	0.00	2.47	0.31	1.07	1.42	1.06	0.06	0.00	0.45	0.27
20	0.00	2.09	0.25	0.70	0.94	0.87	0.06	0.00	0.39	0.22
21	9.75	24.66	2.72	5.69	7.81	10.28	0.00	0.00	3.59	2.05
22	1.30	2.89	0.67	0.87	2.03	1.02	0.00	0.00	0.62	0.42
23	40.45	61.58	2.30	6.11	8.53	3.35	0.43	0.15	3.09	2.12
24	0.78	1.17	0.52	0.85	1.62	1.33	0.10	0.08	0.85	0.71
25	2.55	3.06	4.74	8.96	7.03	3.04	0.59	0.29	2.31	3.56
26	0.52	0.63	0.52	0.63	1.08	0.74	0.16	0.10	0.47	0.90
27	74.12	33.28	8.99	24.22	5.20	6.31	1.01	0.64	1.32	4.97
28	0.26	1.30	1.43	2.11	1.70	1.15	0.20	0.26	0.83	0.81
29	14.07	28.93	8.23	14.52	13.60	11.01	2.01	1.99	5.34	6.16
30	1.46	1.88	0.49	0.96	0.93	0.79	0.17	0.16	0.43	0.50
31	8.18	14.32	4.60	9.68	11.59	10.23	2.28	2.45	4.08	4.90
32	0.89	1.42	0.51	0.46	0.68	0.40	0.10	0.09	0.19	0.25
33	1.93	2.89	0.88	1.81	3.02	2.48	0.36	0.46	0.76	1.10
34	1.30	5.99	0.23	0.45	0.70	0.48	0.17	0.00	0.47	0.53

APPENDIX 3

PUBLICATIONS

C. Robinson, G.B. Shimmield & K.M. Creer
Geochemistry of Lago Grande di Monticchio (southern Italy)
In: 'Paleolimnology of European Maar Lakes'
(Springer Lecture Notes in Earth Sciences 49)

GEOCHEMISTRY OF LAGO GRANDE DI MONTICCHIO, S. ITALY

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ABSTRACT

This account describes the results of bulk geochemical analysis on the uppermost 15m of a 51m profile obtained from Lago Grande di Monticchio. This section is thought to extend from historic times back into the late Pleistocene, hence including the glacial-Holocene transition.

One of the clearest changes seen occurs in the organic carbon content of the sediment, rising from modest values in lower parts of the core to values as high as 30wt% at around 8m depth. In this zone, thought to be correlated with the glacial-Holocene transition, other elements vary directly (Br) or inversely (Al, Y) with organic carbon concentration. Multivariate techniques such as principal components analysis have been used to help identify these elemental associations. Such groupings are suggested as reflecting different contributors to the sediments (eg. plant matter, clays, residual minerals.) The stable isotopic composition of organic carbon displays something of a shift towards lighter values across the glacial-Holocene transition zone, but the profile as a whole is difficult to interpret without further information on the nature of the organic matter. Several elements (P, Mn, Mo) exhibit enrichments in discrete temporal zones and it is thought that these are indicative of diagenetic processes occuring in the sediment.

INTRODUCTION

Lake sediments can provide a detailed record of environmental change. The physical and chemical properties of the sediment reflect developments in the lake ecosystem and changes in rates of process (eg. weathering) around the lake catchment. Also, biotic material contained within the sediments provides indications of change in the local ecology. Lake sediment geochemical studies concerned with long records of deposition (>100,000 years) are relatively unusual in the literature. Exceptions include work on

Lecture Notes in Earth Sciences, Vol. 49
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Paleolimnology of European Maar Lakes

Lac du Bouchet in France (Truze, 1990) and on Lake Biwa in Japan (Horie, 1972-1981).

Lago Grande di Monticchio lies at 650m altitude in the Vulture region, east of Naples. Sediment cores covering a 51m deep profile were recovered from the site during September 1990. The material obtained is well preserved.

It is possible that the sequence from Lago Grande di Monticchio covers the last 250,000 years, almost continuously (Watts & Huntley, unpubl. work), though more lines of evidence would be desirable for confirming this age. This work forms part of an ongoing PhD project, the aim of which is to undertake a comprehensive geochemical study of the whole sequence. In the future this can be integrated with parallel studies (incl. diatoms, paleomagnetism, palynology and sedimentology) to recreate an overall picture.

GENERAL LITHOLOGY

The uppermost 15m broadly consists of laminated muds and gyttjas. A brown diatom gyttja (0-5m) passes down into black, highly organic mud (5-8.4m.) The latter contains localised patches of vivianite up to 1cm in size. Below 8.4m the sequence continues with laminated olive-grey muds. Occasional horizons rich in plant material (mostly mosses) occur here and are up to 2cm in thickness.

Tephra layers are found throughout and provide useful stratigraphic markers. They are of varied compositional nature and range from >20cm in thickness to microscopic horizons not readily detectable.

SAMPLING AND ANALYSIS

Material was taken from Cores C and E which cover the first 15m. Sampling was made at approximately 10cm resolution, providing 159 data points. Owing to the high water content of the top sediments, large continuous quadrants had to be removed from the cores in order to provide sufficient material for all analyses. The sediment was dried for several days at 50°C and ground for 75 seconds in a tungsten carbide mill. This provided a homogeneous fine powder on which subsequent analyses were based.

X-ray fluorescence (XRF) was carried out using pressed powder and fused glass discs to measure trace and major element concentrations respectively. Total carbon and nitrogen were determined on a Carlo Erba element analyser. The samples were boiled with phosphoric acid and the amount of carbon dioxide evolved measured pressometrically. This provided a measure of the inorganic (carbonate) carbon content. By subtracting these values from total carbon a measure of the organic carbon content was found. Biogenic silica was determined using an alkaline wet-chemical leaching technique (Eggimann et al, 1980.) The silica content of the resulting solution was found using a

modified colorimetric method (based on Eggimann et al, 1980.)

Around 30 samples were selected for isotopic analysis of the organic carbon present. A quantity of ground sediment was washed with an excess of 1M HCl to remove inorganic carbon present. Up to 60mg of a treated sample was placed in a silica tube together with an excess of copper oxide. The tube was evacuated and roasted overnight at 850°C. The carbon dioxide produced was purified on a vacuum line apparatus by means of cryogenic distillation. The purified gas was collected in another tube and transferred to a gas-source mass spectrometer. The ratios measured are relative to the PDB standard.

DATA ANALYSIS

With over 30 parameters determined on each sample, it would be convenient to reduce the amount of data viewed while maintaining maximum information on how the complete data set varies. For example, organic carbon and bromine (Fig. 2) show very similar profiles and could perhaps be grouped together into an association reflecting organic matter in the sediments. Multivariate methods of data analysis, principal components analysis (PCA) and correspondence analysis (basic and detrended), were applied in an attempt to eliminate redundancy in the data and to identify a smaller number of associations. The results obtained are best displayed graphically (Fig. 1.) This is an example of R-mode analysis using the PCA method. It shows how the two main axes of variance divide elements measured on Cores C and E into fields and groupings. A number of possible associations can be stated:

a) -the tight clustering of C, N and Br is related to organic matter (plants and animal soft parts)

b) -a band or arch of elements extending from Mg to Ba may represent incompletely weathered igneous minerals (eg. pyroxene), clays and heavy minerals (eg. zircon)

c) -biogenic silica represents contributions from diatom productivity

d) -inorganic carbon reflecting the presence of calcite and/or siderite

e) -Rb, K and Na may be associated with feldspars/feldspathoids, especially in tephra derived material

f) -a broad group of elements (U, Zn, Mn, P, Fe, V, Mo) are largely derived from minerals locally, but show an association with organic matter and may reflect the influence of diagenesis upon the sediment

Axis 1 accounts for 54% of the variance exhibited by the dataset and appears to separate biological vs. minerogenic inputs to the sediment. Thus, the largest differences in sediment nature depend on the relative contributions from these two sources. Axis 2 accounts for 12% of total variance and appears to divide elements strongly influenced by diagenesis from more residual or immobile elements.

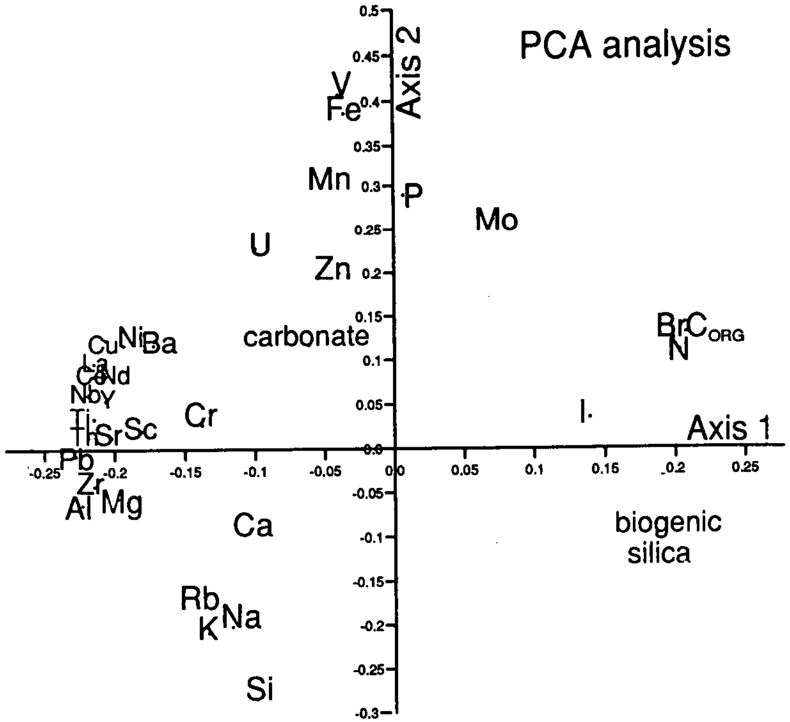

Fig.1. Results of PCA analysis on the data

The three techniques used on the data all produce similar groupings, albeit with some minor variations. In Q-mode it is possible to classify the samples into different facies with moderate success. Without pushing interpretations too far, it is apparent that the elements measured show potential for tracing different sedimentary factors.

RESULTS AND DISCUSSION

The sediment geochemistry may be discussed in terms of terrigenous clastic, biological and diagenetic aspects, with some overlap.

Clastic material is mainly supplied by surface runoff and mass movement within the crater area. This is augmented by sporadic inputs of volcanic material or tephra fallout. There may be some clastic material transported from further afield by aeolian processes, for example during the more arid glacial times. Productivity within the lake (diatoms, algae, macrophytes, ostracods, etc.) and terrestrial inputs of plant debris and pollen contribute to the biological aspect of sedimentation. These primary inputs may be affected by diagenetic processes such as the degradation of organic matter and the release/enrichment of trace metals. Obvious examples of this are the presence of vivianite and siderite.

BIOLOGICAL MATTER

Many lake sediment studies have considered organic carbon to be the most important geochemical variable. Mackereth (1965; 1966) was one of the first to measure a wide range of elements on sediments from the English Lake District. In a series of lakes he found that the carbon content rose rapidly after the cessation of glaciation to reach a maximum in the first half of the post-glacial period. Similar patterns have been found in many other settings (Brown, 1991; Truze, 1990.)

Organic carbon values (Fig. 2) are relatively low, but increasing gradually, between the oldest sediments at 1500cm and 850cm. Around 850cm values increase sharply, reaching a maximum at 450cm, before decreasing somewhat towards the top (most recent) part of the profile. The negative spikes are samples rich in tephra and are organic poor. These pervasive tephra layers add noise to underlying climatic signals.

The rise in carbon around 850cm probably reflects increased productivity or vegetation growth in and around the lake, in response to a more humid and perhaps warmer climate. Terrestrial vegetation development will at the same time stabilise the crater slopes. Reduced erosional activity dilutes the amount of clastic input which will also be seen as an *apparent* rise in organic content. Thirdly, as phyical sedimentation declines the lake waters will stratify more easily (Truze, 1990.) With nutrient enrichment due to enhanced weathering, high internal productivity could lead to anoxic conditions. This too could cause higher organic contents through favoured preservation of matter.

Initial discussions with other groups working on Monticchio suggests that 850cm may be close to the start of the Holocene. This depth is comparable to that found for the Holocene boundary in an earlier palynological study (Watts, 1985) made on a littoral core. It is possible that the actual transition is near 750cm. In this case, the area from 850cm to 790cm is reflecting a late-glacial interstadial, with an intervening period of climatic deterioration between 790cm and 750cm. Such an interpretation requires palynological and dating evidence for support.

C/N ratios can assist in defining the nature of the organic matter (Stuermer et al, 1978.) The C/N values (Fig. 3) rise from around 5 at 1500cm to a maximum of 12 at 1350cm, before dropping back to 5 at 1150cm (with some fluctuation.) From 1150cm to 750cm

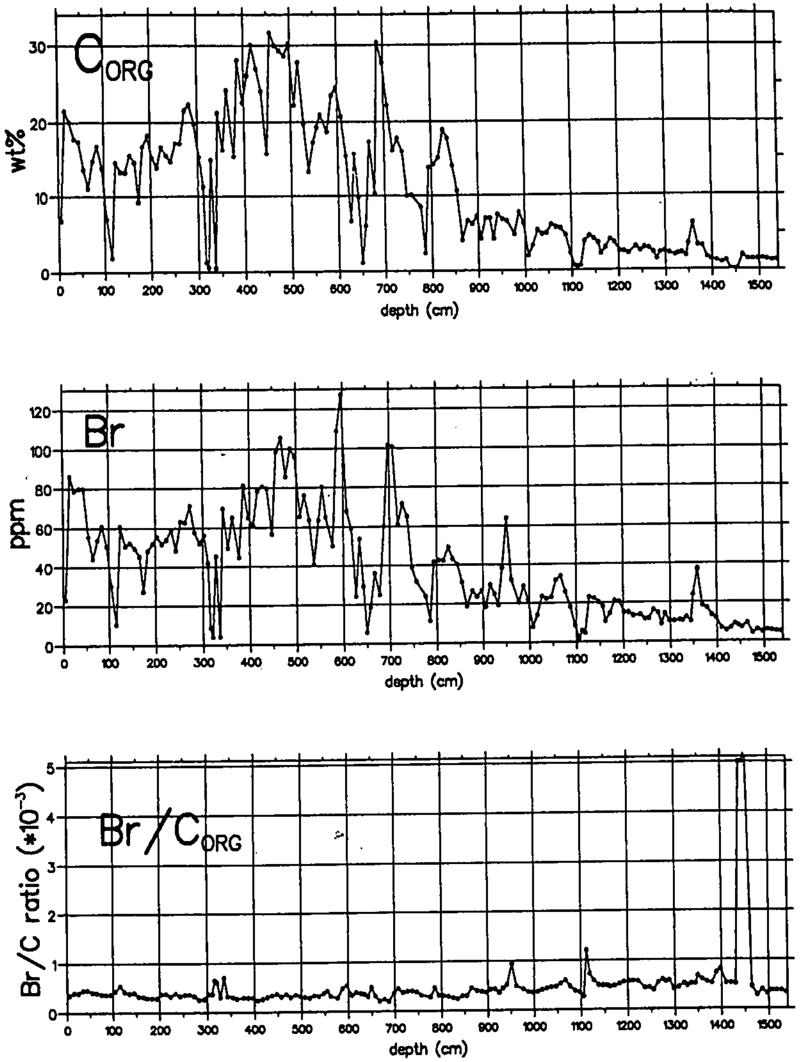

Fig. 2. Organic carbon, bromine and bromine/carbon ratio.

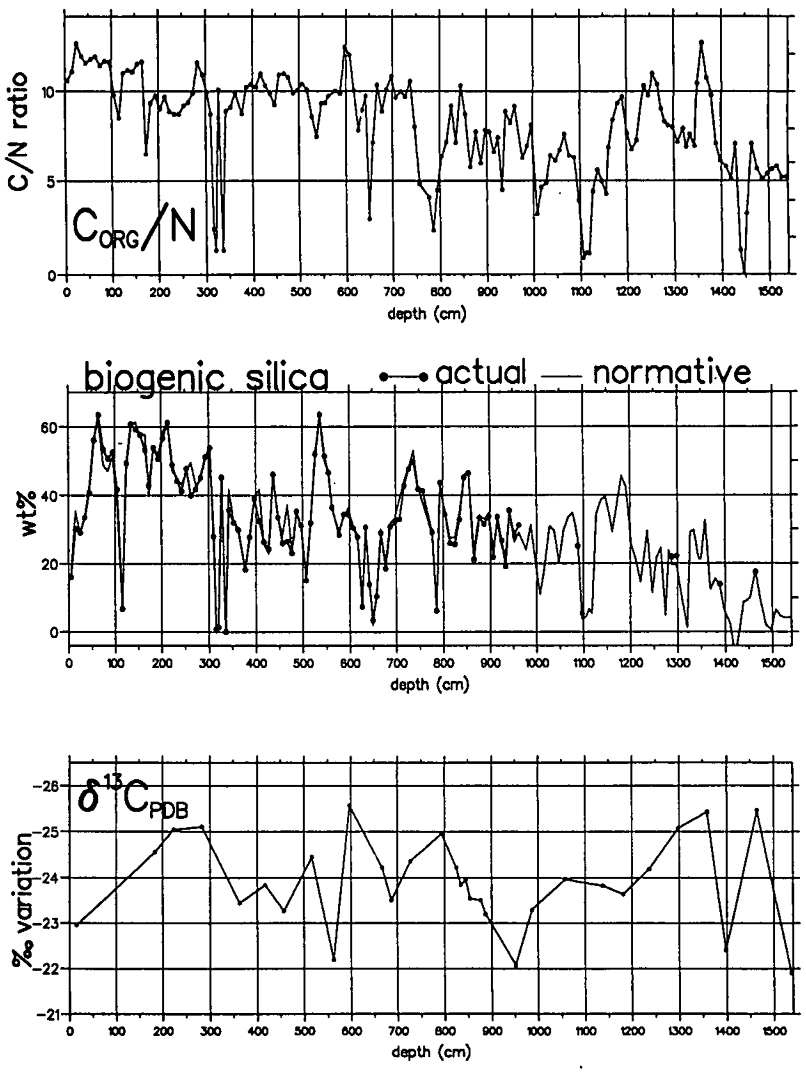

Fig. 3. Carbon/nitrogen ratio, biogenic silica and stable carbon isotopes.

the ratio rises gradually towards 10. Above this depth, values remain high at between 9 and 12. Again, tephra-rich samples impose negative spikes on the overall trend.

The shifts to lower ratios could indicate a change to organic sedimentation dominated by algae and diatoms (Horie, 1972/1977). Lower organisms have ratios of 6-7 as they are rich in proteins. Subsequent rises could signify an increasing influence from higher plant material.This is more cellulose-rich and can have ratios >20. It is likely that the organic matter present is a complex mixture from more than one source. It is not clear why the tephra samples should drag the ratio to such low values. An organic-poor component should dilute organic C and N to similar degrees.

Such interpretations are complicated by the possibility of diagenesis preferentially removing nitrogen during organic degradation. This has been observed in marine environments (Stevenson & Cheng, 1972.) Conversely, as *total* N is being measured, the presence of inorganic nitrogen, can create artificially low ratios (Mackereth, 1966; Muller, 1977.) Therefore if a sediment is organic poor, but contains a small quantity of inorganic N, for example in the form of fixed ammonium, a low ratio would be detected. This could explain the negative tephra spikes although further investigation is needed.

Bromine and organic carbon are strongly correlated (r=0.938). It is known that sediments are enriched in Br due to the presence of plant material (Cosgrove, 1970) and that the element is concentrated in humic layers of soils (Vinogradov, 1959.) Since most Br is believed to arrive through ocean-derived aerosols, the Br/C ratio has been thought to reflect "oceanicity" (wind conditions, etc.) of the atmospheric/climatic system by some workers (Mackereth, 1966.) It could also reflect change in the type of organic matter deposited or processes of diagenesis and recycling. Examination of the Br/C ratios on the material under study (Fig.2) shows that marginally higher ratios occur between 850cm and 1450cm. Thus, if the ratio depended *only* on rate of halogen supply from rainfall, the ocean may have had more influence on local climate during this earlier period. Positive spikes associated with tephra samples show that these layers have excessively high bromine contents in proportion to their low organic carbon values.

Actual biogenic silica results correlate well with a normative biogenic silica calculated using XRF major element oxide data:

$$\text{biogenic silica} = SiO_2 - 2.8 * Al_2O_3$$

This calculation assumes that total silica is composed of a biogenic component and a minerogenic/aluminosilicate component. The factor of 2.8 selected is lower than an average shale silica:alumina ratio of 3.4 (Turekian & Wedepohl, 1961), but fits the sediment type from these cores better. Actual and normative values are plotted on the same axes for comparison (Fig. 3.) As the actual measurement of biogenic silica is time consuming it was decided to continue with a smaller number of selected samples below 970cm in order to verify the accuracy of the XRF estimation.

Results bear some comparison with elements reflecting organic matter. From 1500cm to 750cm there is a rise from 5% to 50% total sediment composed of biogenic silica, with local troughs (tephra layers) and peaks present. Above 750cm values peak briefly at 540cm and are high for a longer phase between 300cm and 50cm.

It seems likely that diatom productivity has contributed appreciably to the sedimentation throughout most of the time period covered by these cores. Over the upper half of the sequence the sediment is almost entirely made up of amorphous silica and organic matter. Here, the relative dominance of these two components varies with time. This may result from the changing role of diatoms and other plant and algal life in the lake productive system.

Fig. 3 shows the results of stable isotopic analysis on bulk organic carbon in the sediments. Since the 1960's possible relationships with environmental changes have been investigated. Håkansson (1985) reviews a series of factors which could contribute to variation in the isotopic ratio and presents results from Swedish lakes. In these sediments a marked decrease in $^{13}C/^{12}C$ coincided with the glacial to post-glacial transition. This shift to isotopically lighter carbon has also been found in Meerfeldermaar, Germany (Brown, 1991) and to some extent in Lac du Bouchet (Truze, 1990.) On the other hand Nakai (1972) associated more temperate periods with heavier isotopic ratios, as did Stuiver (1975.) Harkness and Walker (1991) observe a superficial correlation between ^{13}C enrichment and climatic change, but identify features which do not correlate with a simple climatic relationship.

The carbon isotope values determined on Lago Grande di Monticchio vary between -25.5 and -22‰. This could be said to typify a fairly average mix of lacustrine organic matter. When compared with the element information it is sometimes difficult to relate the fluctuations seen with apparent environmental changes. For example, between 950cm and 750cm there appears to be a pronounced shift, but beyond this values fluctuate without clear explanation. The probable Holocene section contains both high and low points. Further study of the organic matter and palaeobotanical data would help with the interpretation. Ideally it would be more informative to look at isotopic variations within individual organic compounds (Rieley et al., 1991.)

The lack of a coherent shift in isotopic values could result from the lake's southerly location. Perhaps the vegetation associated with some of the northern European sites suffered more climatic stress between glacial and interglacial periods. It is also possible that autochthonous organic matter is profoundly influenced by the lake water bicarbonate reservoir. This could modify the expected ratios if a majority of plants are assimilating carbon from this source. These results emphasise the local differences between individual lakes.

TERRIGENOUS CLASTIC MATERIAL

Many of the elements measured are associated almost exclusively with the minerogenic sediment fraction (Al, Zr, K, etc.) Fig. 4 shows how Al and Y contents vary. Between

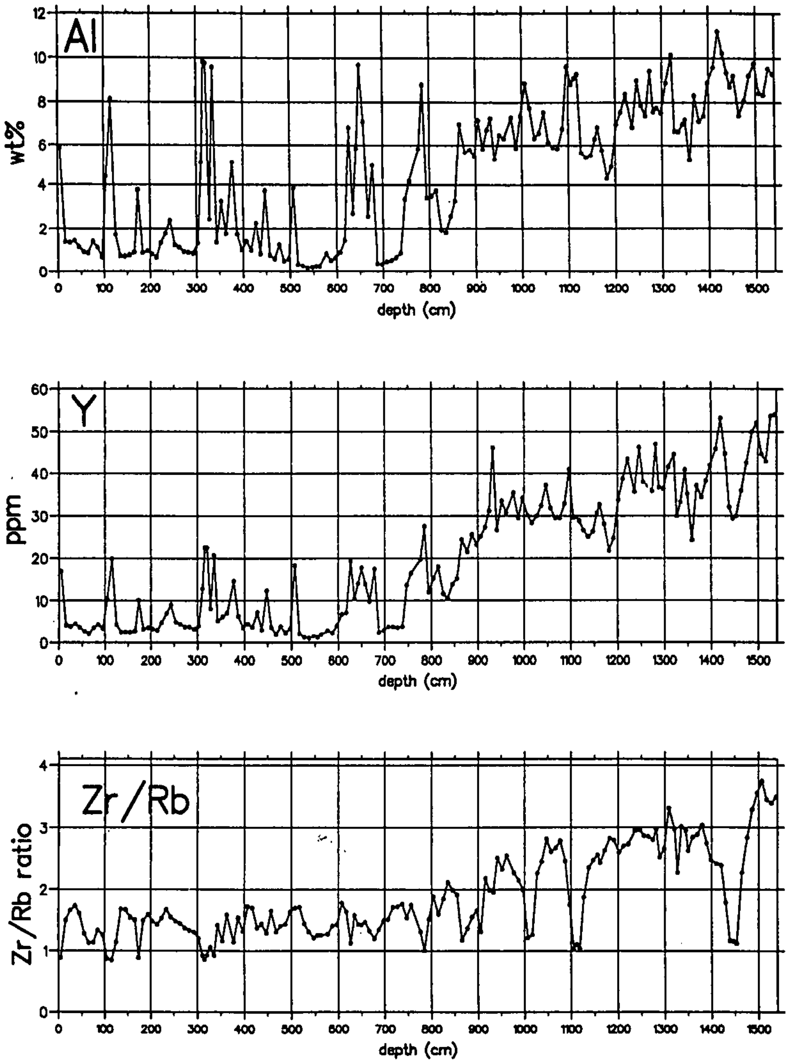

Fig. 4. Aluminium, yttrium and zirconium/rubidium ratio.

1500cm and 850cm concentrations are decreasing gradually, with a slight step downwards at 1200cm. At 850cm values drop sharply, but return a brief maximum over the next 100cm. From 750cm to the top the concentrations are very low, but tephra layers add positive spikes to the general pattern. A minimum seems to be reached at 540cm after which there is a gentle increase towards more recent times.

If the amount of clastic material sedimented has fallen this could be interpreted as being due to: (1) reduced erosional and transportational processes and (2) a dilution effect from increased organic sedimentation. The major control on this is believed to be slope binding or stabilisation arising from terrestrial vegetation development.

The surrounding volcanic rocks are composed of pyroxenes and feldspathoid minerals with smaller quantities of apatite and oxides present. X-ray diffraction analysis suggests that a certain amount of pyroxene and apatite finds its way into the sediment. Mineralogical analysis is difficult where the material is so dominated by organic matter and amorphous silica. Clay minerals are probably present too, though they are proving difficult to extract for identification. Quartz has been identified in a few samples from the lower parts of the sequence. This mineral may be derived from outside the crater area. The tephra layers tend to include feldspars, such as sanidine, along with some pyroxene and apatite.

Ratios such as Zr/Rb have been used to identify change in grain size (silt/clay) of the clastic material sedimented (O'Donnell, 1987.) Results (Fig. 4) show a decrease from Zr/Rb ratios of 3.5 at 1500cm to 1.5 at 700cm. From 700cm upwards the ratio remains steady at close to 1.5. This suggests a gradual coarsening of grain size below the probable Holocene base. Some tephra layers give negative spikes which could reflect their geochemical nature (relatively alkali-rich compared to zircon content.) Since the tephra represent coarse grained layers they might otherwise be expected to add strong positive spikes to the curve.

DIAGENETIC FEATURES

Some examples of diagenetic effects are touched on in this section. An immediate feature from visual examination is the presence of vivianite at around 600cm depth in the black gyttja. This has been recognised as a diagenetic precipitate in a wide range of lake sediments (Mackereth, 1966; Nriagu & Dell, 1974; Truze, 1990.) Fig. 5 shows enrichments in P, Fe and Mn between 500cm and 700cm. Thus vivianite appears to be concentrated in a discrete time zone, thought to represent the early Holocene, rather than being found throughout the Holocene. Nriagu & Dell (1974) considered the precipitation or dissolution of phosphate to act as a buffer, regulating phosphorus levels in the interstitial waters and release to the overlying lake waters. Formation is often associated with anaerobic decay in organic-rich sediments. Phosphorus might be derived from organic matter releasing nutrient phosphate or from mineral/skeletal apatite decomposition. During the early Holocene conditions within the sediment may have

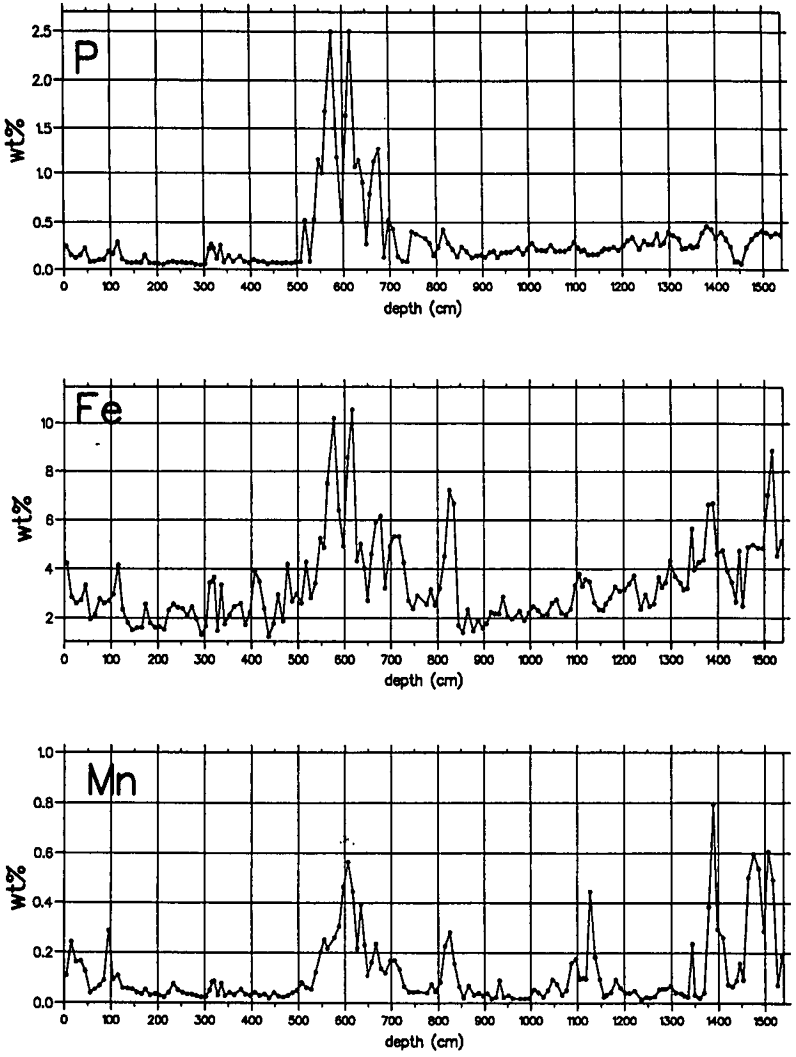

Fig. 5. Phosphorus, iron and manganese.

changed to reducing in nature and this might have converted large quantities of ferric iron to the more soluble ferrous form. Upwards migration of pore waters (aided by sediment compaction) could lead to high concentrations of both Fe^{2+} and phosphate in near surface sediments and cause vivianite to precipitate. Perhaps after this boundary period later organic accumulations have not had access to sufficient iron to allow more vivianite formation. Other mechanisms are undoubtedly possible.

The Mo profile (Fig. 6) shows a pronounced enrichment (<90ppm) between 850cm and 800cm. Above this horizon concentrations decline exponentially towards the 10ppm level. The element is known to accumulate in living plants owing to its physiological properties, such as biocatalysing nitrogen fixation (Bortels, 1930.) However, the enrichment observed has probably been enhanced through diagenetic processes. Two of

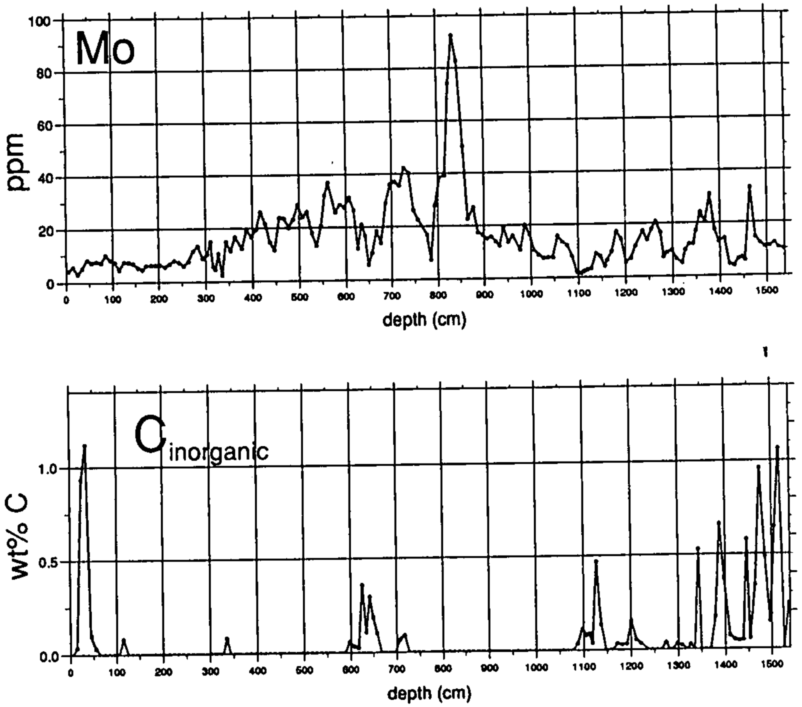

Fig. 6. Molybdenum and carbonate carbon

the major mechanisms of uptake are coprecipitation with Fe sulphides and fixation by adsorption or reduction in organic rich sediments. The former is possible as sulphide contents are believed to be elevated (from preliminary investigations.) The area of enrichment is also one of high organic carbon content and was earlier suggested to represent a late-glacial interstadial event. A change to reducing conditions in the sediment at this boundary zone (and resulting migration/fixation of Mo from underlying sediments) might be invoked in similar manner to the early Holocene-vivianite explanation. The zones of phosphate and molybdenum enrichment occur in different time planes illustrating how elements may respond differently to the conditions of diagenesis.

Carbonate carbon (Fig. 6) is present at certain levels, with XRD analysis identifyng the presence of both calcite and siderite. These are probably of diagenetic origin, although ostracods found below 1500cm (Wansard, pers. com.) show that skeletal bioclastic carbonate occurs lower in the sediment column. XRD results suggest that the area between 10cm and 50cm contains calcite along with some gypsum. Between 100cm and 1150cm in the sequence the carbonate occurrences tend to be associated with tephra samples. It is not clear whether carbonate minerals have arrived with the tephra fall or whether the influxes of alkaline volcanic material have increased the pH value of the lake water favouring temporary carbonate precipitation. Towards 1500cm carbonate contents are not associated with tephra inputs and must reflect longer term physico-chemical conditions in the lake, such as evaporation and P_{CO_2}. Elevated Fe concentrations occur in this lower region, where siderite is more prevalent. Mn is also higher and is probably substituted in the carbonate. This contrasts with the Fe and Mn enrichment associated with phophate at higher levels.

CONCLUSIONS

These initial geochemical results reveal a wide variety of trends with much opportunity for further explanation. A basic division can be made between the upper half of the section (rich in organic matter and biogenic silica) and the lower half (containing modest amounts of the latter two components and an increasing amount of clastic material.) The added presence of diagenetic phases (vivianite, siderite, etc.) in discrete temporal zones could further help in reconstructing environmental conditions. Influxes of tephra could have a marked impact on what otherwise may be a climatically controlled regime.

It is hoped to continue this characterisation through the whole 51 metres of succession. Investigation of specific components of the sediment, such as organic geochemical studies, will give insight into problems less readily explained by bulk analysis. Dating methods are now required to aid the interpretations made.

ACKNOWLEDGEMENTS

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