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Lago Grande di Monticchio, southern Italy: a long record of environmental change illustrated by sediment geochemistry

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Abstract

Bulk geochemical analysis has been carried out on a 51-m sediment core from Lago Grande di Monticchio in southern Italy. The record, which may extend from the present back through more than one glacial cycle, displays major variations in indicators of palaeoproductivity such as organic carbon and biogenic silica. The most prominent change occurs at the Holocene boundary. Lower in the sequence, zones of moderately enhanced productivity highlight either interstadial or interglacial periods. C/N ratios and hydrogen indices provide possible indications of the sources and diagenetic state of the bulk organic matter, but must be interpreted carefully as it is difficult to isolate the effects of these two factors. Changes in the clastic fraction (e.g., Na/Al ratio) suggest that tephra deposition in the lake and its catchment has significantly altered the sedimentation. This may also have influenced the biological productivity of the system.

1. Introduction

Long records of lacustrine sedimentation (>20,000 yr) extending back from the present are relatively unusual. They 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 Myr has been recovered and its geochemistry studied (Horie, 1984; Meyers et al., 1993). Relatively small crater lake sites occur in many volcanically active parts of the world. These lakes have an average lifetime of up to several hundred thousand years and so extant lakes will probably be associated with volcanism during the last 1 Myr. Lago Grande di Monticchio, a crater lake in southern Italy, has been examined under the Commission of European Communities supported "EUROMAARS" programme. The aim of this programme has been to reconstruct the European Quaternary record in detail over the most recent glacial cycle(s). A classic multidisciplinary approach has been adopted with parallel investigations in palynology, varve microstructure, ostracods, palaeomagnetism and tephrochronology. This paper deals with the results of geochemical investigations of the bulk sediment composition. Using modern techniques it has been possible to recover multielemental data on a large number of samples. The extent to which this may be used as a palaeolimnological tool will be demonstrated. At present, the level of interpretation is

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limited, particularly because of the absence of a reliable age model. The question of sediment chronology forms an integral part of the geochemical discussion.

2. Site location

The Laghi di Monticchio are situated in a caldera of the Monte Vulture volcanic massif (15°36'E, 40°56'N) approximately 120 km east of Naples. Lago Grande lies at an altitude of 656 m above sea level and is presently separated from the smaller Lago Piccolo by a 5-m bar. The surrounding Vulture complex has been studied both in terms of its geomorphological evolution and its petrology. It is generally considered that the lake(s) formed sometime after 500,000 yr B.P. when the main cone building phase ended (Capaldi et al., 1985; de Fino et al., 1986; Guest et al., 1988). Recently Laurenzi et al. (1993) have presented an Ar–Ar date of 130,000 yr which they associate with the formation of the Monticchio lakes. The authors advised that this single, preliminary date should be treated with caution and further information is awaited. The bulk of the volcanic sequence is composed of foiditic and tephritic fall, flow and surge deposits with interbedded lava flows. The Vulture sequence is 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).

Lago Grande has a present surface area of 0.4 km^2 and an approximate catchment area of 2.4 km^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 during times of high rainfall. 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-m marginal terrace zone in prehistoric times (see Watts, 1985), then the catchment/lake surface area ratio would be even lower (perhaps <3). Lago Grande has a maximum depth of 34 m, but much of the lake is a shallow shelf sloping gently from the shoreline towards 12-m depth (Hansen, 1993). This asymmetric profile contrasts with the more simple cauldron shape usually encountered in maars. It is thought that the shallow shelf area of Monticchio reflects a level of sediment infill that has reached a mature stage.

The lake is probably spring fed and thus regulated by the local groundwater system. This would appear to subdue lowering of water level caused by the Mediterranean summer (B. Huntley, pers. commun., 1993). It might be argued from this that major lake level changes at the site would require permanent alterations to the tectonic–hydrological system or at least long-term climatic changes. Productivity is presently eutrophic to polytrophic (B. Zolitschka and J.F.W. Negendank, in prep.) with high densities of macrophytes in the shelf zone and a greenish water colour caused by algal blooms.

The catchment consists of a steep crater whose slopes support a stable cover of mainly beech and oak. The fourth side of this crater opens into a valley which is at present dry. 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. Unfortunately, the soils have not been sampled or studied, although they appear at first sight to be thick and well established. According to a European atlas of soils (FAO–Unesco, 1974), the Monticchio region is associated with soil type "Bea-*1/2*ad". This is an Ando-eutric Cambisol (by definition of volcanic origin) and *may* reflect characteristics of the parent rock as much as prevailing climatic regime (Duchaufour, 1982). Such soil types may vary from the young, base-rich and eutrophic state to a more developed humic-allophane complex state with substantial losses of bases and immobilisation of phosphorus by aluminium.

3. The core

During September 1990, a "EUROMAARS"-supported team recovered a series of cores penetrating just over 51 m of sediment from under 6 m of water in the shelf area. Operations were carried out using a modified Livingstone (piston) corer mounted on a raft (Livingstone, 1955; Usinger, 1991). A previous core had been taken in the deep cauldron zone of the lake under 30-m depth of water. However, coring was abandoned at this location owing to the chaotic and inpenetrable nature of the sediments.

The top of the 51-m sequence is nominally taken as 0 cm, but in fact the sediment–water interface is a further 40 cm above this. The sediments are described in detail by Zolitschka and Negendank (1993). The sequence consists of laminated muds and gyttjas with occasional layers of coarser material. In the upper sections a brown diatom gyttja (0–500 cm) grades into black, highly organic mud (500–850 cm). The latter contains localised patches of vivianite up to 5 mm in size. The upper 850 cm represent the most organic-rich zone in the profile and have a distinct pulpy or gelatinous texture as well as high water contents (>80 wt%). Below 850 cm the sequence continues with laminated pale brown or olive-grey muds. These occasionally grade into darker and more organic-rich zones, but not of the same quality as the upper 850 cm. Horizons rich in plant material (mostly mosses) occur locally and are up to 2 cm in thickness. These are particularly noticeable between 900- and 1900-cm depth. The sequence is interrupted by a relatively coarse and clastic-rich zone of silty "turbidites" between 1900 and 2120 cm. Two slump units, both over 1 m in thickness, are found at 2200- and 2800-cm depth. Tephra layers are found throughout and provide useful stratigraphic markers. They appear of varied composition and range from >20 cm in thickness to microscopic horizons. Positive indicators for lake desiccation or emergence, such as soil or peat horizons, evaporite deposits or oxidised layers have not been observed. This suggests that the sediment record may be more or less continuous. It is 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. commun., 1992).

4. Materials and methods

After the cores had been recovered they were transported to Trier University (Germany) where they were extruded. While the material was in prime condition all core sections were subsampled for later geochemical analysis. Sampling was carried out at an approximately 10 cm resolution employing continuous chunks of wet sediment to provide sufficient material for all the analyses. The samples were dried for 48 hr at 50°C and ground for 75 s in a Tema® mill. Analyses of major and trace elements were made by X-ray fluorescence spectroscopy (XRF) using fused glass disc and pressed powder preparations, respectively. Samples were analysed on a Philips® PW *1480* spectrometer. Total carbon and total nitrogen were determined on a Carlo Erba® NA-*1500* elemental analyser. Inorganic carbon was determined by a simple pressometric method, similar to G.A. Jones and Kaiteris (1983). Organic carbon was estimated by difference using the total and inorganic carbon results. Biogenic silica was measured on selected samples using an alkaline (2 *M* Na_2CO_3) leaching technique coupled with spectrophotometric determination of the molybdenum blue complex. The method followed was essentially that described by Eggimann et al. (1980). Hydrogen index measurements were made on selected samples by pyrolysis, using a Leco® THA-*200* Thermolytic Hydrocarbon Analyzer. The precision on each of these measurement techniques was in general found to be within ±5% or better. For further details the reader is referred to Robinson (1993).

5. A sediment chronology problem

A fundamental requirement in this type of study is the existence of a reliable sediment chronology. So far, attempts at radiometric dating have not yielded reliable results. Bulk radiocarbon dates made on the core appear excessively old. This problem was also encountered by Watts (1985) and may be due to a hard-water effect (perhaps related to volcanic emissions of CO_2) and/or the presence of substantial reworked carbon which is being washed in from the catchment. Unfortunately, radiocarbon-dated bryophyte fragments have also given unreliable dates which do not even form a concordant stratigraphy. The results of Ar–Ar dating work on several tephra layers are awaited in the future. It may also be possible to obtain some reasonable guide as to the chronology from varve examinations which require several more years to complete.

The Holocene–glacial transition is widely accepted as lying around 750-cm depth in the record. This correlates well with Watts' (1985) work on a previous marginal core. However, for deeper parts of the sequence there currently exist two possible age models:

(1) the core covers up to the last 70,000 yr with the zone from 2700 to 3400 cm representing a 35–50,000-yr *interstadial* and the 4900-cm zone representing a minor interstadial some time after the well-known St. Germain II interstadial (Stage 5a). In this case there are no earlier interglacial periods recorded and the last glacial period is highly detailed — the "young alternative", or

(2) the core covers the past 200–250,000 yr and thus includes the Eemian *interglacial* (Stage 5e) at 3400 cm and a preceding *interglacial* which might correspond to oxygen isotope Stage 7 at 4900-cm depth — the "old alternative".

These two models have arisen through the correlative approach made by groups working on the 1990 core sequence. Of the different correlations, that of palaeomagnetism does not appear to provide an unambiguous result (Turton, 1992) and the tephrochronological investigations require further work (Newton and Dugmore, 1993). Thus palynology has provided the main guide. These results (Watts et al., in prep.) highlight a period of enhanced arboreal pollen between 2700- and 3400-cm depth which to some extent "mirrors" Stage 5 of the marine oxygen isotope profile. However, the possible interglacial signature here is questionable because the magnitude of these indicators is significantly below that of the Holocene (which would be expected to represent type interglacial conditions).

6. Results and interpretation

With over 30 elemental parameters determined on each sample it was decided to apply a multivariate data appraisal to help qualify the main sources of variance and to eliminate redundancy. Use of principal components analysis highlighted an important variance between biogenic and terrigenous contributors to the sediment (Robinson et al., 1993). The following presentation will be structured in terms of elements associated with these two main components. Other elements measured (e.g., Fe, Mn, Ca, P, Mo) show significant associations with authigenic components, but their discussion will be left to a future paper (C. Robinson and B. Zolitschka, in prep.).

6.1. Organic carbon

Many studies have considered organic carbon to be the most important geochemical variable (Mackereth, 1966). An association between rise in organic carbon content and climatic improvement has been found in many lacustrine records, but care must be taken in the widespread extrapolation of this relationship which may be strongly influenced by local factors. If the Monticchio profile is examined (Fig. 1), values appear relatively low (<4 wt%) between the oldest sediments at 5100-cm up to around 1500-cm depth. Between 1500 and 860 cm, values increase gradually towards 7 wt% C. Above 860 cm, there is a sharp rise to much higher organic carbon contents, and from here to the surface values remain consistently above 15 wt% C. An immediate feature in this upper zone is the presence of a number of pronounced negative spikes. These are due to tephra layers covered in the sampling profile.

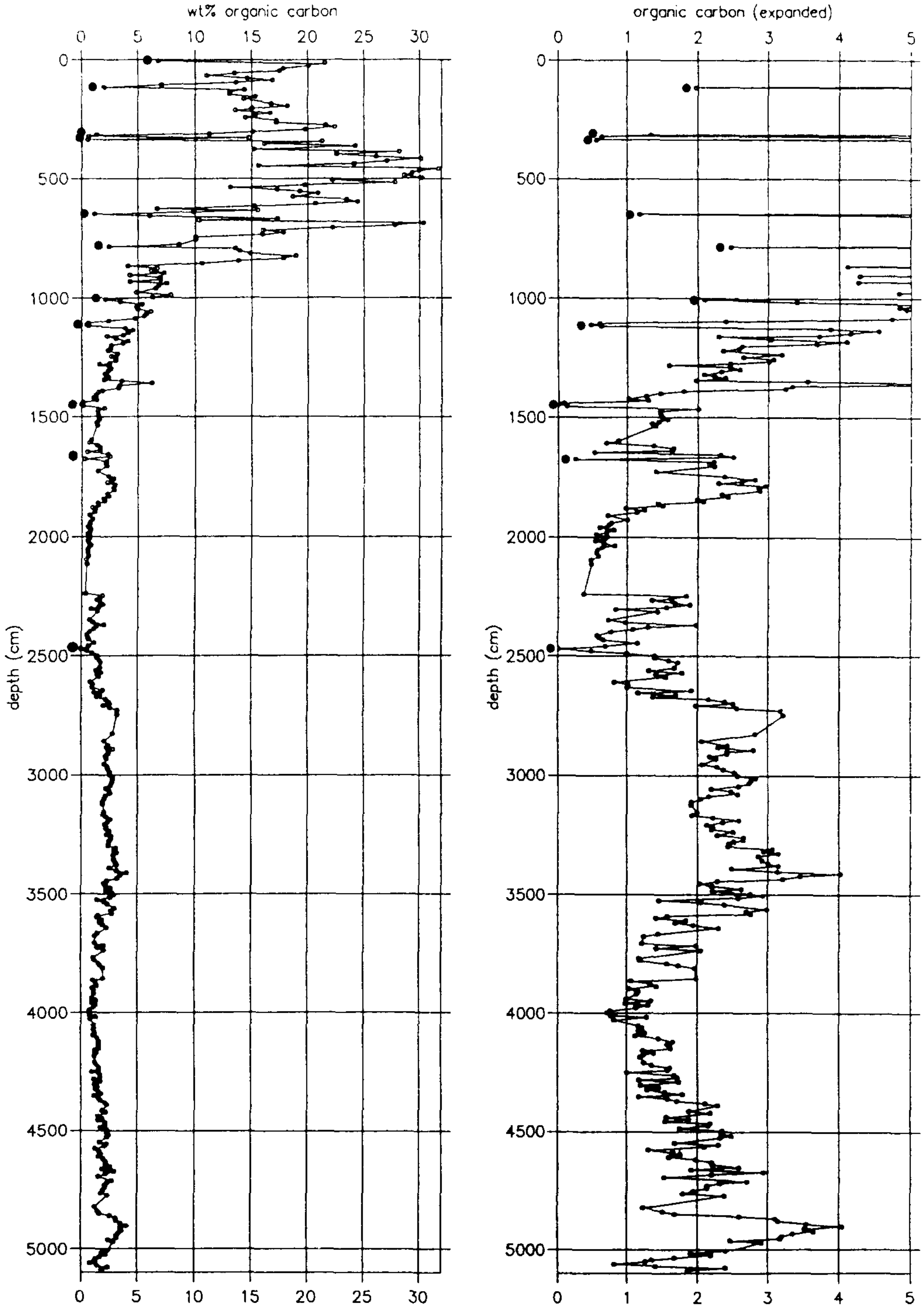

Fig. 1. Organic carbon content. (Tephra *dominated* samples are indicated by *solid circles* in this and subsequent figures. It should be noted that many other samples contain some tephra material.)

The pervasive presence of tephra layers adds noise to a potential underlying climatic signal.

Organic carbon *content* is affected by: (1) productivity; (2) preservation; and (3) dilution. Within lakes, as in marine environments, increased productivity is generally considered to arise through increased nutrient availability (Tissot and Welte, 1984; Birks, 1986), and to a lesser extent by light or temperature increases. Climatic, edaphic (soil related) and morphometric factors may each have a direct or indirect effect upon nutrient availability (Carpenter, 1983). Terrestrial productivity in the catchment zone is influenced by edaphic factors and more directly by climate. Although widely ranging values for organic decomposition exist, it is thought that in many organic lacustrine muds the bulk of mineralisation takes place within the first few centimetres of the sediment–water interface (Lovley and Klug, 1986; Herczeg, 1988; Wersin et al., 1991). Interpretations of long lacustrine records have tended to emphasise that the primary control over organic carbon content is productivity rather than preservation (Meyers, 1990; Brown, 1991; Talbot and Johannessen, 1992). 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 800 cm and then drop sharply over a short interval. Thus the present record will be interpreted in terms of productivity being the driving force, although it is recognised that variations in preservation through time may impose a secondary effect. To evaluate the effects of dilution by other components on the organic carbon content requires accumulation rate data. Although these rates cannot be calculated, it is possible to make reasoned interpretations using the age models available and knowledge of the environmental setting.

From work on Lac du Bouchet, Central Massif, France, Truze (1990) provides a useful model to explain the increases in organic carbon accumulation during periods such as the Holocene as compared with glacial times. Briefly, as terrestrial vegetation increases in response to a more humid or warmer climate the slopes of the crater catchment area become stabilised. The ensuing reduction in erosional activity reduces the amount of clastic deposition which may be seen as an *apparent* rise in organic carbon concentration. Moreover, weathering processes become dominant and increased nutrients leached from the soil lead to high productivity within the lake. 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 35,000 yr B.P., represented "intermediate environmental regimes" between these end-members.

At Monticchio the rise in organic carbon above 860 cm probably reflects such a response to a more humid and perhaps warmer climate. As mentioned, it is thought that this level is close to the start of the Holocene. Alternatively, if the actual transition is near 750 cm, the area from 860 to 800 cm might reflect a late-glacial interstadial (Bølling–Allerød event?), with an intervening period of climatic deterioration (Younger Dryas?) between 800 and 750 cm. Evidence of the Younger Dryas signal being observed in lake sediment geochemistry has been demonstrated in Alaska, U.S.A. (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, the zone between 800 and 750 cm does appear to contain a peak in steppic vegetation (J.R.M. Allen, pers. commun., 1993), but supporting evidence from varve counts is awaited. The negative spikes in organic carbon content associated with tephra layers 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.

The organic carbon record from 860 cm to the base of the sequence at 5100 cm may be interpreted in alternative ways according to the two age models previously presented. A central question regarding this interpretation is: "Do we expect the Eemian interglacial to show similar levels of organic carbon (reflecting productivity) as the Holocene?" With the *young age interpretation*, the more organic-rich area between 2700 and 3400 cm in Monticchio might correlate with a 35,000-yr interstadial period seen in Lac du Bouchet (Truze and Kelts, 1993) The last glacial maximum might be considered to lie around 2000 cm where organic carbon values decrease to < 1 wt% for several metres. The area from here up to 860 cm would thus be interpreted as the last deglaciation. If correct, it would appear that the last deglaciation contains an early period of enhanced productivity at 1800-cm depth which is followed by a drop to low productivity around 1500 cm before productivity rises again towards the Holocene. This trend cannot be compared with known climatic records which typically show a monotonic improvement during the last deglaciation.

The *old alternative* involves correlation of the area between 2700 and 3400 cm with the Eemian interglacial and St. Germain I and II events. The area at 4900 cm is more speculatively correlated with an earlier interglacial around 220,000 yr B.P. In this interpretation, the organic poor area at 2000 cm in Monticchio is hypothesised to be the product of dilution by a prolonged phase of clastic input to the system which may have arisen through factors other than climate (e.g., volcanic disturbance). The actual last glacial maximum may be represented around 1200-cm depth. This could permit the organic carbon peak at 1800 cm to be correlated with an interstadial event of around 35,000-yr age. With this interpretation it is necessary 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, involving factors other than climate. This subject will be returned to in the discussion section.

6.2. Biogenic silica

Like organic carbon, biogenic silica content offers a (more specific) guide to past biological productivity. Microscopic examination reveals that diatoms occur in large quantities throughout virtually the whole core (B. Zolitschka, unpublished data, 1992). This phenomena is probably a reflection of the lake's volcanic setting (cf. B.F. Jones and Bowser, 1978; Martin et al., 1992). During the determination of actual biogenic silica (Robinson, 1993) it was found that the early results correlated extremely well with a normative model for biogenic silica calculated from the XRF major-element data:

$$(\text{biogenic silica}) = SiO_2 - 2.8 * Al_2O_3 \quad (1)$$

The factor of 2.8 selected is lower than an often quoted "average shale" silica/alumina ratio of 3.4 (Turekian and Wedepohl, 1961), but fits the possibly more aluminous sediment type from this core better. As the actual measurement of biogenic silica is time consuming it was decided to continue with a smaller number of selected samples below 970 cm in order to verify the accuracy of the XRF estimation model. Comparison of the two curves (Fig. 2) shows that below 970 cm some discrepancy occurs and negative estimations of biogenic silica are seen at 2000- and 4000-cm depth. This must be due to changes in the silica/alumina ratio of the 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. However, the normative model above offers an adequate high sampling 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.

The biogenic silica profile below 2000-cm depth (Fig. 2) shows broadly comparable trends to organic carbon content, but the signal from the biogenic silica record is more accentuated. For example, the zone around 3400 cm which may

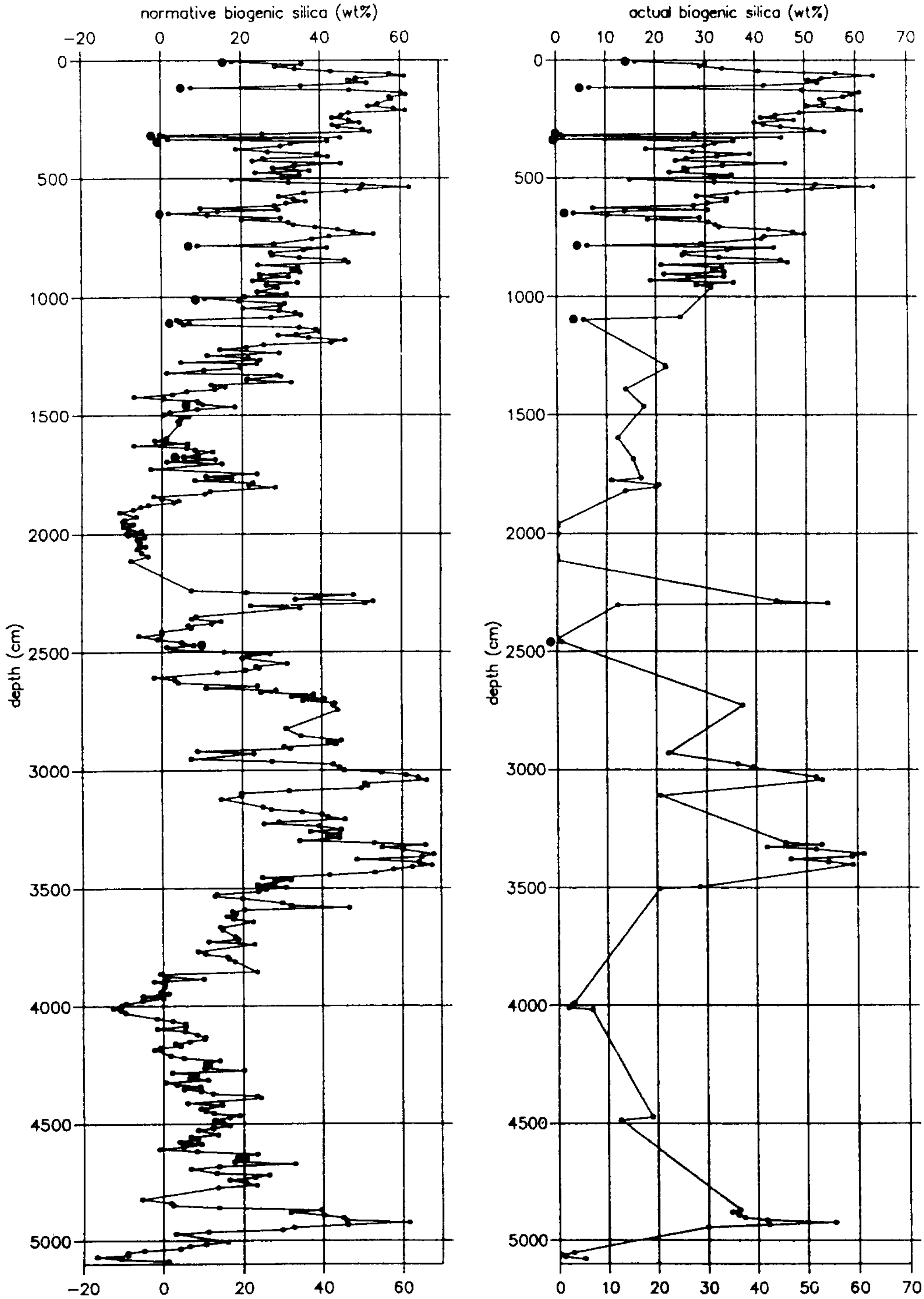

Fig. 2. Normative and actual biogenic silica content.

represent the Eemian interglacial (according to the old age model) shows biogenic silica contents of 60 wt%, while values drop to effectively zero at 2000-cm depth. Microscopic examination has shown that diatoms *are* present at 2000 and 4000 cm in very low numbers (B. Zolitschka, unpublished data, 1992). The biogenic silica record also appears to pick out more clearly possible interstadial events at 2600- and 2300-cm depth. The latter period again records very high levels of biogenic silica over 50 wt%.

Above 1000 cm biogenic silica varies more independently with respect to organic carbon and the two parameters only correlate closely where tephra layers cause dilution. From 1000 to 780 cm biogenic silica content remains around 30 wt% with two fluctuations towards higher values over 40 wt%. The possible Younger Dryas zone (800–750 cm) does not suffer a significant decline in biogenic silica outside the brief interference of a coeval tephra layer at 785 cm. This contrasts with marked declines in organic carbon and C/N ratio (see Section 6.3) in the same zone. During the early Holocene biogenic silica is generally lower at around 30 wt%, although peaks at 750 and 540 cm show brief periods of very high values. Above 350 cm, values rise to a sustained high for the next 300 cm and range from 40 to 60 wt% SiO_2. In the most recent part of the Holocene, above 50-cm depth, there appears to be a pronounced reversal and values decrease sharply towards the present. These changes are thought to reflect relative patterns of dominance between the main groups of plankton in the lake (diatoms, green algae, etc.).

Increased availability of nutrients will 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 progressively higher water temperatures green followed by blue-green algae became dominant.

The interpretation of biogenic silica may be related to Truze's model mentioned earlier. It is suggested that sedimentation during the earlier part of the record (below 2000-cm depth) took place under conditions of lower nutrient (in particular P) availability, although supply of silica from mature catchment soils may not have been as reduced. Under these conditions diatoms could outcompete other planktic groups and 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 interglacial (or interstadial) periods at 3400 and 4900 cm when enhanced terrestrial vegetation cover favoured the leaching of slightly higher levels of nutrients from the catchment area. The change is reflected by dramatic rises in biogenic silica content, although the response of organic carbon content (representing overall productivity) is more subdued. During the sedimentation record above 2000-cm depth, a renewed nutrient supply from freshly leached volcanic material deposited on the catchment (see below) could have caused an increase in the supply of phosphorus relative to silica. This may have culminated during the optimal conditions of the Holocene and latest-glacial periods, causing the dominance of diatom contributions to be reduced and reflected by the more subdued trends in the biogenic silica profile.

6.3. C/N ratio

In this study, the C/N ratios reported refer to the weight ratio of organic carbon to *total* nitrogen. The C/N values (Fig. 3) show fluctuations between zero and >17, although most samples lie between values of 5 and 15. The Holocene C/

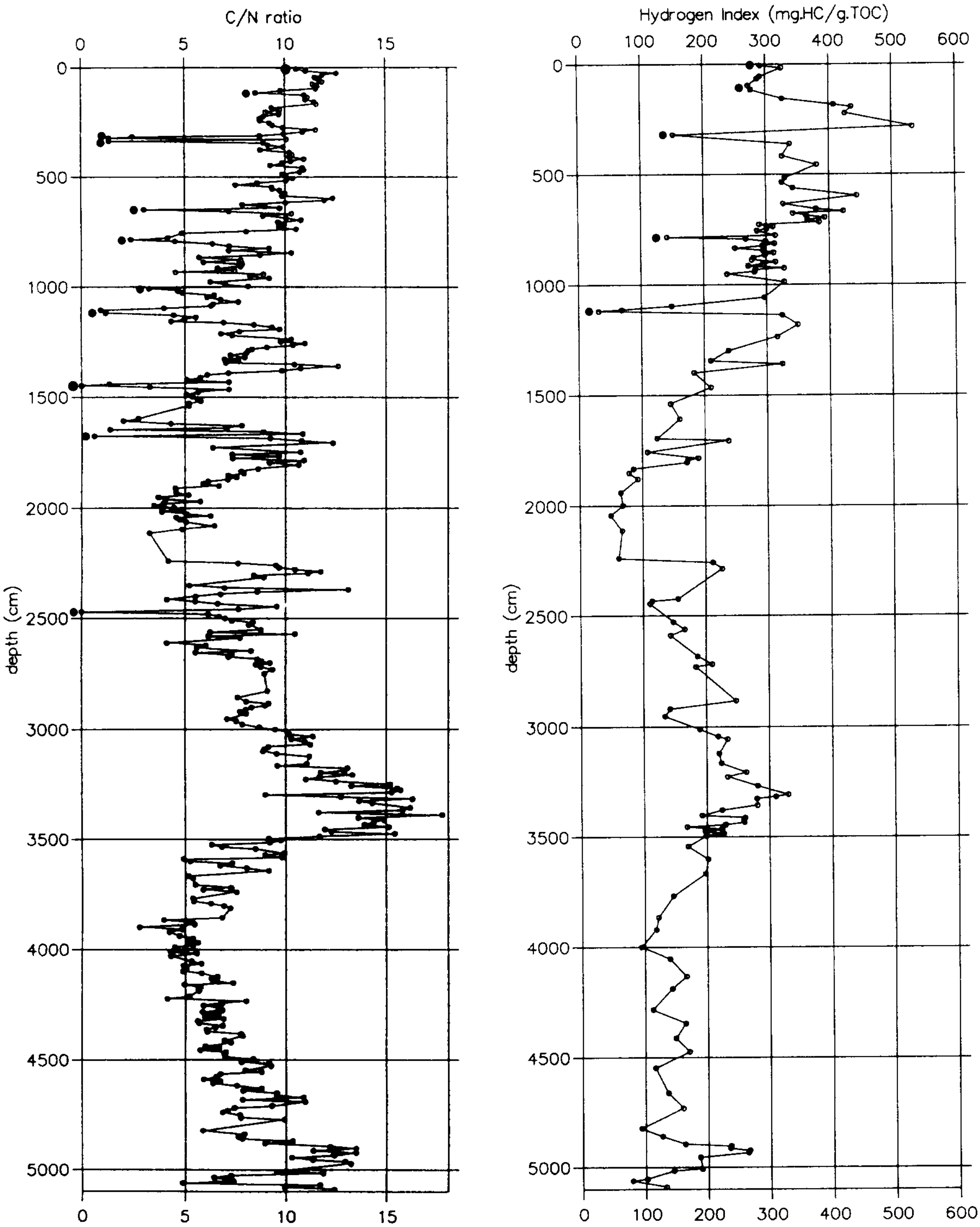

Fig. 3. C/N ratio and hydrogen index values.

N ratios are generally close to 10 and are expected to represent significant contributions from both terrestrial and aquatic lower-plant components. The relative constancy in ratio over perhaps 10,000 yr of sedimentation suggests that the period has not experienced any fundamental changes in the basic organic mixture. The slightly higher values in the upper 150 cm of the profile might be associated with an increase in aquatic macrophytes (high-C/N plants) across the lake shelf. 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, analysis of typical catchment area rocks shows that this primary inorganic material contains virtually no carbon, but up to 0.07 wt% N (Robinson, 1993). 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 certain very low C/N ratios in the core profile.

The fall in C/N to values as low as 5 in the 800–750-cm zone suggests that diatoms or algae have temporarily become the dominant source of organic matter. Comparison with the organic carbon profile shows that a positive correlation exists between the two parameters. This implies that the amount of organic matter supplied by terrestrial vegetation and/or aquatic macrophytes has decreased significantly while the input from planktonic productivity has suffered less (cf. biogenic silica record). Thus there appears to be a sensitive response to climate from productivity in the terrestrial/catchment vegetation zone, but a lower response from lacustrine productivity changes during this possible Younger Dryas period.

Variations in C/N ratio between 2000- and 800-cm depth suggest further changes in the relative importance of terrestrial and aquatic matter, but these details will not be discussed. Below 2000 cm there exist two important maxima at 3200–3500-cm depth and at 4900 cm during the interglacial (or interstadial) periods. Both lacustrine and catchment productivity were probably 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 may 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 3200 cm show relatively low or intermediate values.

The correspondence between C/N ratio and organic carbon content below 2000 cm raises the question of whether inorganic nitrogen may be responsible for the often low glacial C/N ratios (Mackereth, 1966; Muller, 1977). A plot of total nitrogen against organic carbon (Fig. 4) shows a high degree of correlation 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. It is considered reasonable that C/N ratios as low as 5 are related mainly to organic nitrogen components. Nevertheless, it may not be safe to conclude that the C/N ratios reliably reflect the organic matter sources. The organic matter may have experienced some diagenetic lowering of the C/N ratio. This contrasts with the normally encountered increase in C/N ratio (Kuivila and Murray, 1984), 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 would seem necessary to improve the interpretation of the C/N record.

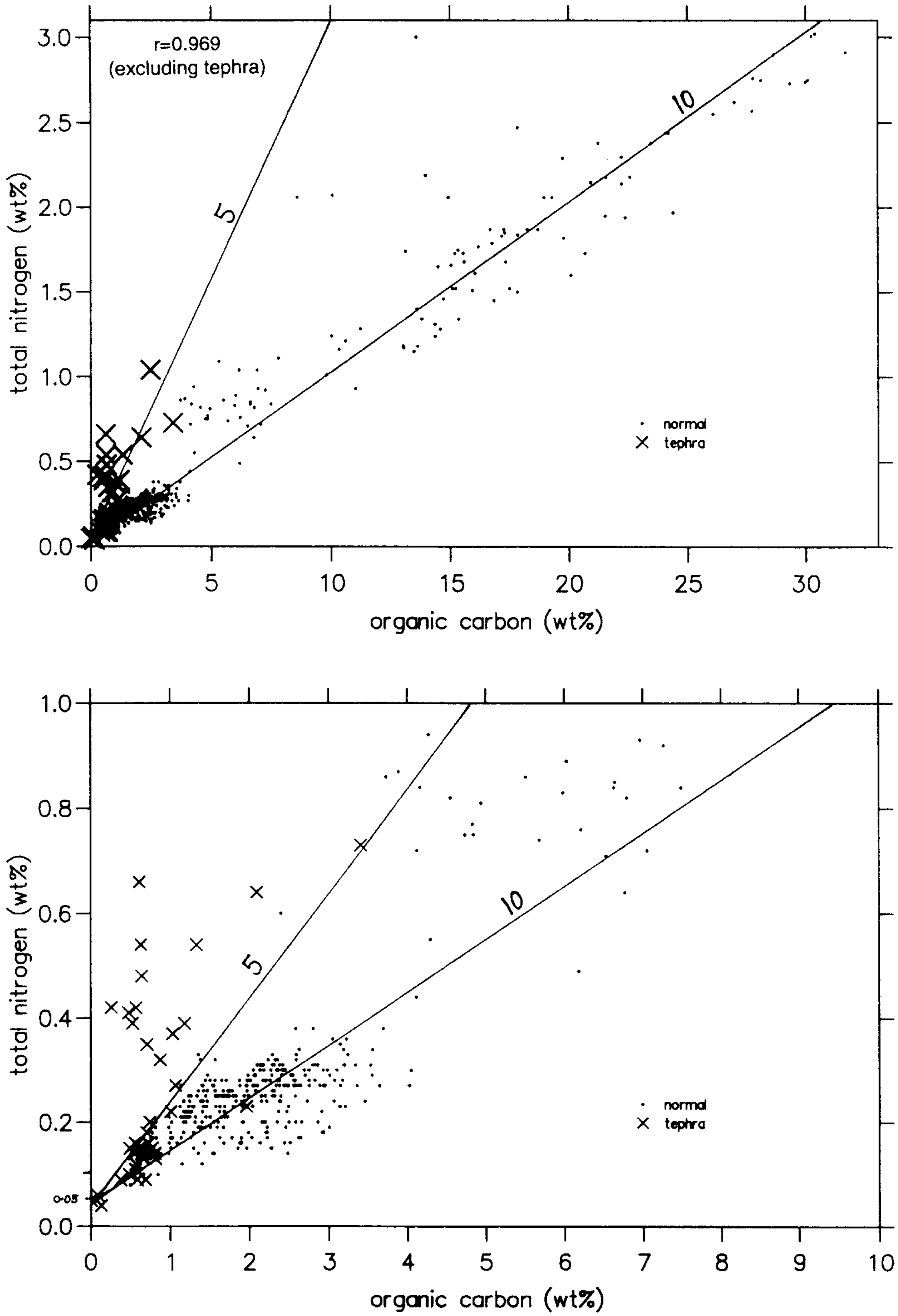

Fig. 4. Total nitrogen against organic carbon content for all samples.

6.4. Hydrogen index

Like C/N ratios, hydrogen index (HI) values can give information on the sources and diagenetic state of the organic matter. They provide an indirect estimate of the atomic H/C ratios of the kerogen component. Previous lacustrine studies have emphasised to varying degrees the relative importance of source and diagenetic factors on hydrogen index (Talbot and Livingstone, 1989; Hollander et al., 1992; Truze and Kelts, 1993). HI-values over 750 are classically related to the presence of a planktonic matter source. However, more recent data have 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. commun., 1993). In the Monticchio record (Fig. 3) the HI profile displays similarities with both organic carbon and biogenic silica with highest values during the Holocene (300–500). A peak occurs at 250 cm at which time biogenic silica content is also maximal. From the C/N ratios it was suggested that the organic matter in the Holocene sediments contains major contributions from planktonic and terrestrial 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 300–500 represent a simple mixture (terrestrial and planktonic) of unaltered sources or a dominant component of partially degraded planktonic matter. Some reworked organic matter from the catchment may also contribute to the modest values observed.

The plateau seen during the glacial–Holocene transition between 750- and 1250-cm depth is in accordance 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. It is thought that the generally low HI-values below 2000 cm are reflective of changes in organic matter preservation as much as source. 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 may be explained if the glacial areas contain low amounts of highly degraded planktonic matter (i.e. of low HI-value) and contain perhaps a significant quantity of humic- or lignin-bound nitrogen. In contrast, the interglacial (interstadial) areas contain higher quantities of both planktonic and terrestrial organic matter which have experienced a better degree of preservation. 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.

7. Terrigenous components

Examination of the sedimentology and mineralogy of the core is being carried out in detail by other groups working on the Monticchio sequence and only basic information is currently available. Preliminary X-ray diffractometric (XRD) mineralogical investigations (G. Irion, unpublished data, 1993; Robinson, 1993) reveal very low concentrations of clastic minerals over large sections of the profile, particularly between 0- and 800-cm and between 3200- and 3500-cm depth. From trial clay suspensions, an illite–muscovite mineral $KAl_4[Si_7AlO_{20}](OH)_4$ appears reasonably abundant around 2000-cm depth and in other areas some halloysite and beidellite are found. Many diffraction traces display a large hump feature around 4.5 Å which is related to amorphous substances. These may include diatom silica, volcanic glass and amorphous clay minerals. Amorphous clays such as imogolite ($SiO_2 \cdot Al_2O_3 \cdot 2H_2O$) and allophane ($1.0–2.0SiO_2 \cdot Al_2O_3 \cdot 2.5–3.0H_2O$) are known to occur in volcanic weathering regimes (Wada, 1987) and *could* represent a significant fraction of the clay mineral assemblage. XRD examination of the bulk sediment shows that the main minerals present are pyroxene, quartz and apatite. These will be concentrated in the silt fraction and probably derived locally. They may survive weathering processes in preference to the feldspathoid and glass components of the local rocks. 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 as xenocrysts. Some quartz may also be of aeolian provenance, but this is difficult to assess.

In studying the clastic mineral fraction it is desirable to avoid additional imprints caused by authigenic processes. With this aim, the current discussion will focus on conservative elements such as Al, Zr and K which are associated almost exclusively with the terrigenous clastic fraction. *Many* of the trace elements analysed show similar behaviour to the major elements (Robinson et al., 1993), but cannot be related to specific mineralogical phases 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 and they will not be presented here.

Concentration profiles for elements such as Al and Y (Fig. 5) indicate how the relative amount of clastic deposition has varied. These elements predictably 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 Al and Y, 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 500-cm depth, above which values rise to slightly higher levels. Clastic content rises sharply below 750-cm depth producing a brief maximum in the possible Younger Dryas period. After a subsequent minimum around 825-cm depth, values rise sharply again to much higher levels over the next 150 cm. Maxima are reached at around 1500-cm depth and lower in the profile at 2000-, 2400- and 4000-cm depths. In these areas the concentrations of Al and Y are around $\times 10$ that in the Holocene.

Decreases in Al or Y could be interpreted as reduced clastic deposition (i.e. diminished erosive and transportational processes) or dilution from increased biogenic sedimentation. Both effects may be operating simultaneously as predicted by Truze's model. Since most of the sediment sequence consists of muds containing fine laminae (< 0.5 mm in thickness), it is thought that the rate of terrigenous inwash has not changed dramatically. Also, the limited catchment area suggests that the primary factor causing change in clastic content is dilution by large increases in biological productivity. However, the tephra layers and the coarse turbidite zone at 2000-cm depth suggest situations where enhanced clastic deposition is the primary control.

Due to the large dilution effects between clastic and biogenic components it is necessary to examine changes in the ratios of elements not strongly associated with the latter in order to investigate the terrigenous clastic composition. The Na/Al ratio has been applied as an index of weathering in lake sediment studies (Mackereth, 1966; 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. An alternative hypothesis to the "record of changing soil compositions" 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 within the same soil system or selective transport of minerals in different particle size classes (Dearing, 1991 and references therein).

The Na/Al profile (Fig. 6) shows that the upper 1000 cm including the Holocene actually contain higher ratios (> 0.1) than the preceding glacial periods (< 0.07). Tephra layers are typically of trachytic composition (Newton and Dugmore, 1993) and are expected to host significant Na in alkali feldspar phases. They impart positive spikes on the record, but values seem to remain elevated for prolonged periods outside the actual tephra horizon. For example, above a prominent tephra at 650 cm Na/Al remains > 0.2

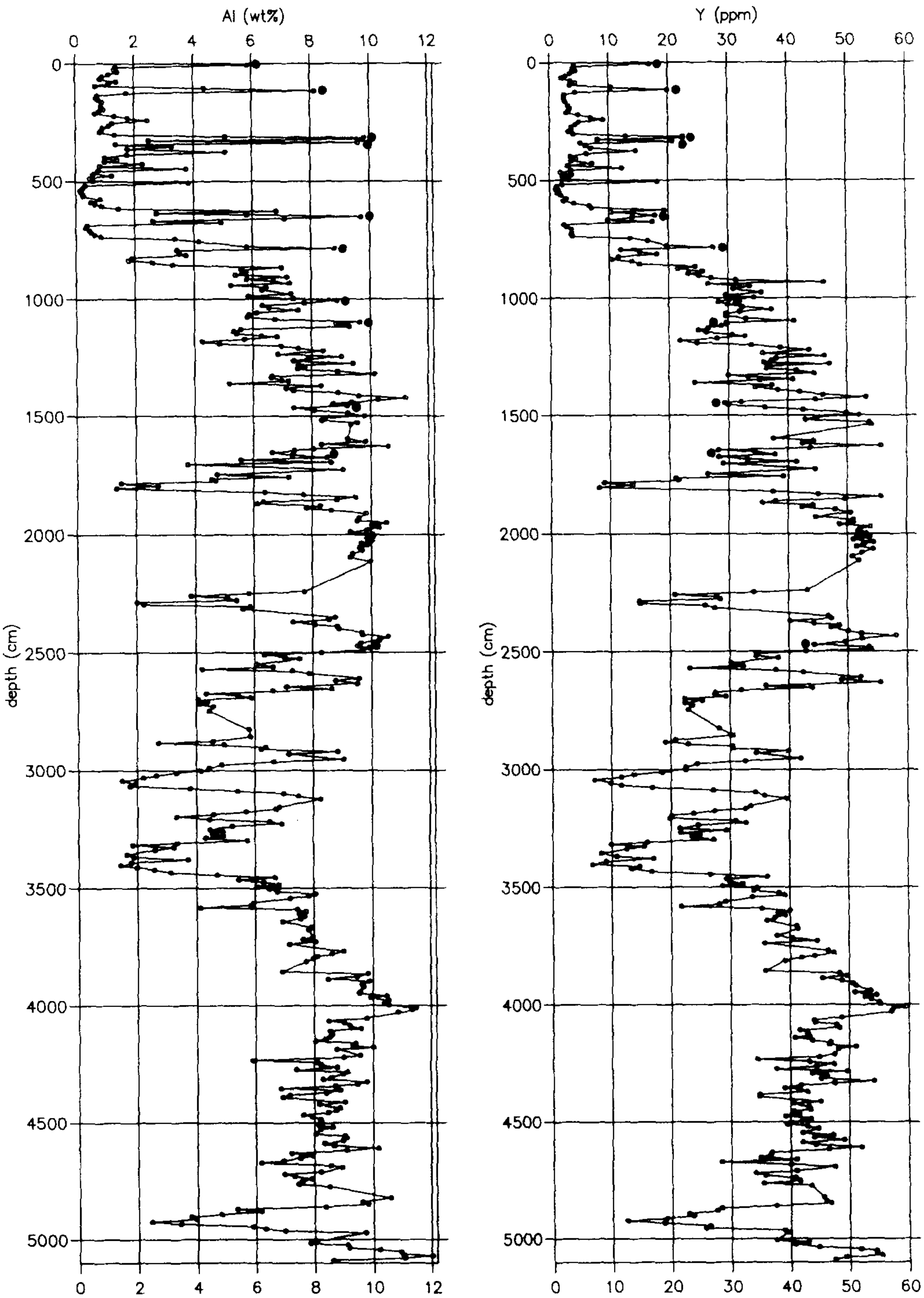

Fig. 5. Aluminium and yttrium content.

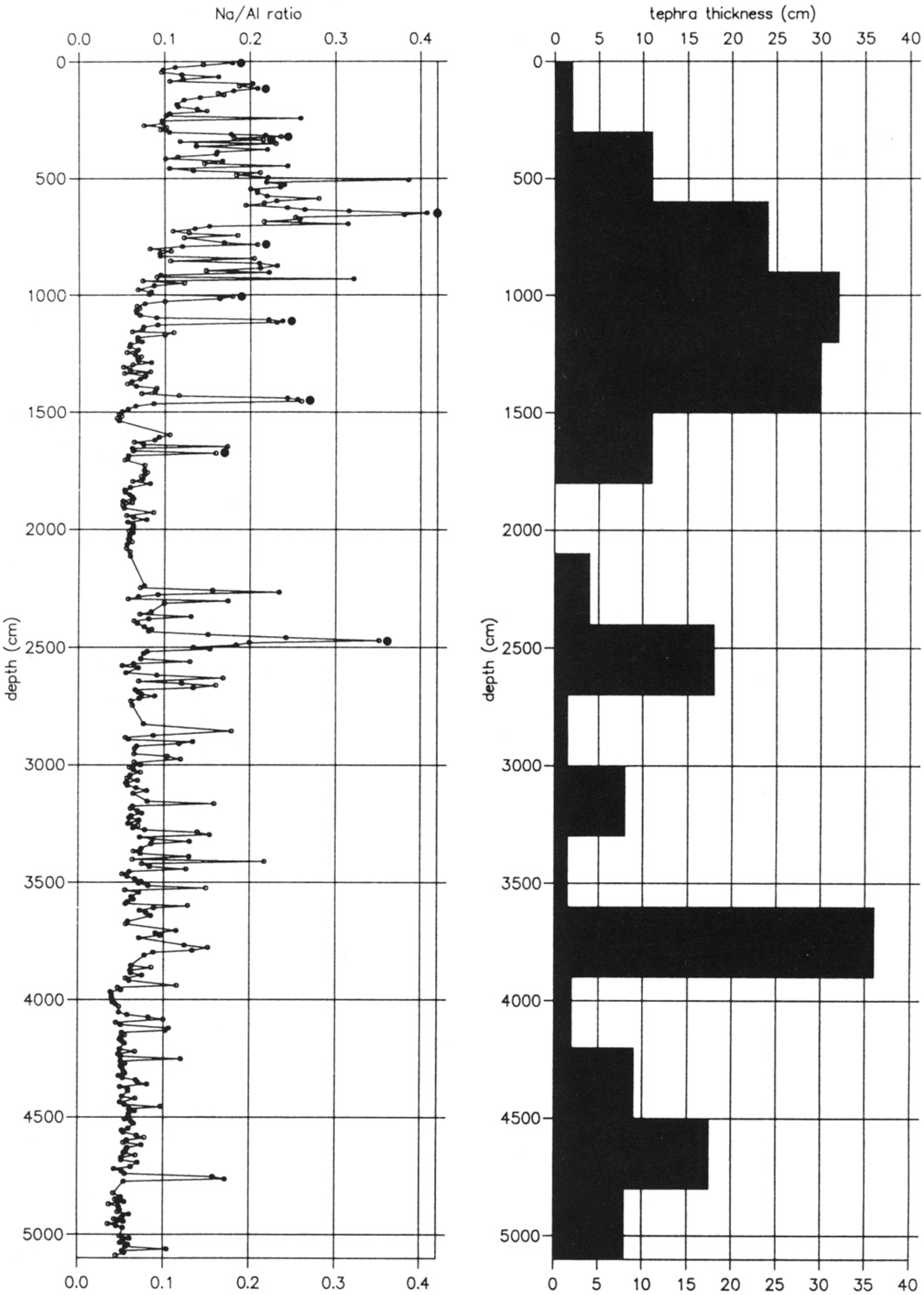

Fig. 6. Na/Al ratio and histogram of tephra thickness per unit depth.

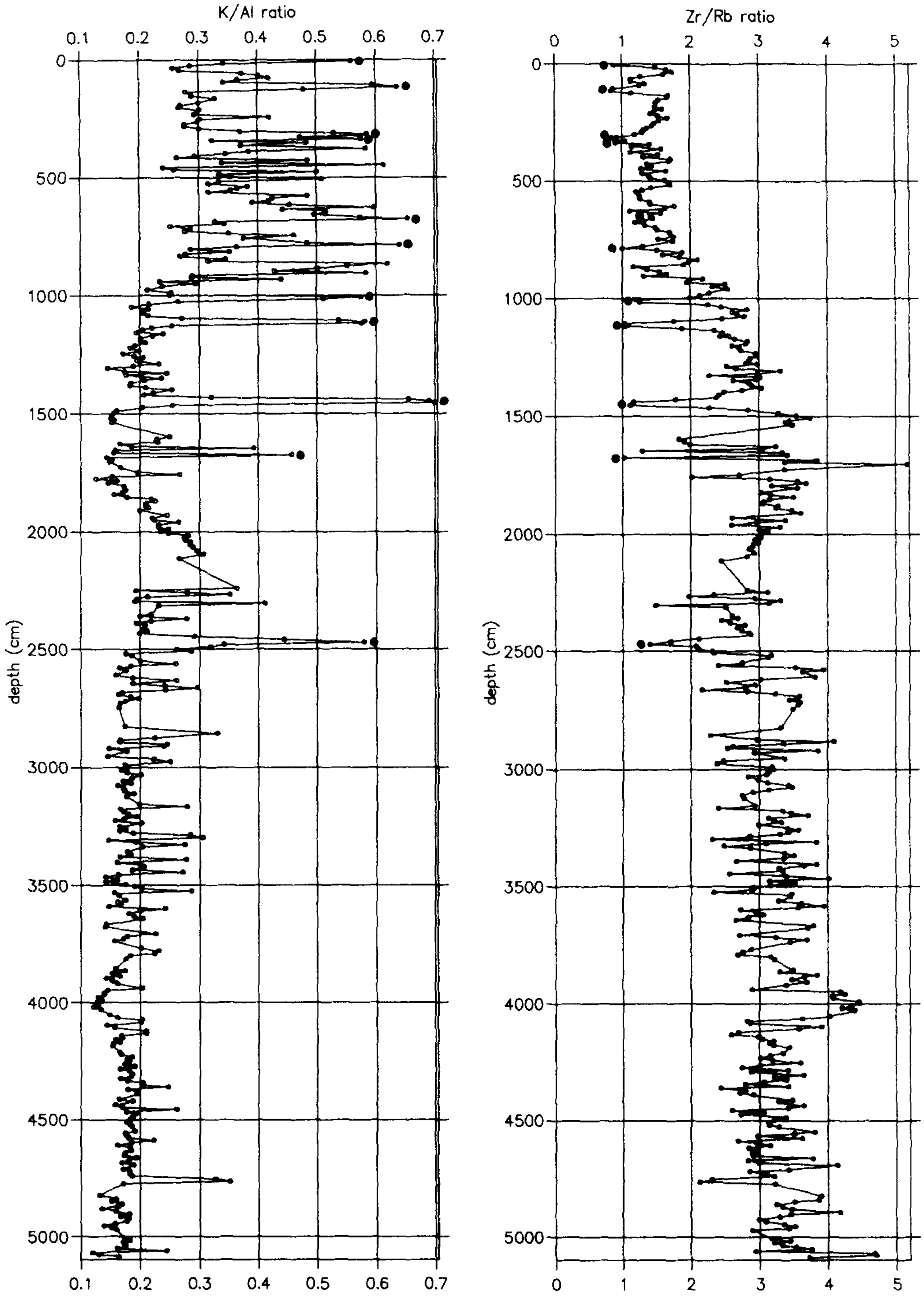

Fig. 7. K/Al and Zr/Rb ratio.

for the next 150 cm. 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. A histogram of tephra thickness (in cm) per 300 cm of sediment was compiled from visual examination of the core. It is shown for comparison beside the Na/Al profile (Fig. 6) and illustrates a major deposition of tephra between 1500 and 500 cm in the record which broadly corresponds to increasing Na/Al ratios seen in the sediment geochemistry. It would seem that possible signals from the catchment weathering–erosive regime (in response to climate) are outweighed by the effects of tephra supply with regards to the clastic material deposited. Under "normal" sedimentation conditions there appears little change in the Na/Al ratio that can be attributed to catchment weathering/erosion. For example, between 2500- and 3750-cm depth relatively few tephra layers are observed and there is little change in the Na/Al ratio from a value around 0.07.

The K/Al profile (Fig. 7) may be interpreted in a similar overall way to Na/Al, although it is noted that a prominent zone of elevated K/Al ratios occurs around 2100-cm depth. This is in the highly minerogenic turbidite region and the elevated ratios are thought to be associated with increased illite contents which may have been brought about by erosion and removal of deeper soil layers in the catchment region. Possible causes for this are mentioned at the end of the article.

The Zr/Rb ratio might be expected to reflect the proportion of silt to clay (zircon/clay minerals) in the sediments. Results (Fig. 7) show that Zr/Rb ratios are relatively high (between 3 and 4) for the lower part of the core up to 1500-cm depth. Between 1500 and 700 cm values decrease progressively towards 1.5. From 700 cm upwards the ratio remains steady at close to 1.5. A primary relationship between Zr/Rb and grain size does not appear to exist since tephra layers (which often represent coarse sandy material) are characterised by negative spikes. Also, the zone of turbidites at 2000-cm depth, which is significantly coarser than the surrounding muds, does not show an elevation above background values for the lower core. It appears that changes in the Zr/Rb ratio are also related to the influence of external tephra inputs which are relatively rich in alkalis as compared with the local weathered catchment. Below 1500 cm 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 700 cm could reflect a shift towards catchment sedimented material which is compositionally influenced by a sequence of tephra falls that have progressively blanketed its slopes.

8. Discussion

The bulk geochemical data presented raise a number of questions which require more specific work to be answered. Nevertheless it may be appropriate at this stage to focus on the central question regarding the significance of the sediments at 2700- to 3400-cm depth. If the sediment geochemistry is dominated by a response to climate (in a similar fashion to Truze's model) then these sediments must represent an interstadial of around 35,000–50,000-yr age. This would appear to agree with extrapolation of the Holocene sedimentation rate of 0.75 mm yr^{-1} to the base of the core. It is to be wondered whether the fluctuations seen in this interstadial might be correlated with, say, the Dansgaard–Oeschger cycles of the ice record. This could only be assessed in the presence of accurate dating controls. Alternatively, correlation with the last interglacial period (Stage 5) would be in accordance with a biogenic dominated sediment system and would imply substantially reduced sedimentation rates in the lower parts of the sequence. The effect of compaction will make some contribution to the apparently lower sedimentation rate, but it is necessary to examine other reasons for the lower productivity (nutrient status) during this earlier time. One possible explanation has already been suggested: it may be that during the earlier period the catchment soils had reached a mature stage and yielded low levels of nutrients to the system. Later, an increasing frequency of tephra falls blanketing the catchment may have altered the surface soils and provided a nutrient load. Such a process has been considered in a number of younger lacustrine records (Haflidason et al., 1992; Einarsson et al., 1993). Another perturbation may be connected with the turbidite deposits (in the form of a local eruption or large earthquake) perhaps exposing fresh soil material. A third possible factor is associated with the gradual shallowing of the lake through sediment infill. Under the more recent shallow water conditions more effective nutrient recycling may have occurred between the internal sediment load and the epilimnion. This would enable greater amounts of carbon to be fixed to the sediments (Binford et al., 1983; Carpenter, 1983). These suggestions may be difficult to test, but remain working ideas while the sediment chronology problem is solved.

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