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The last *ca* 2000 years palaeolimnology of Lake Candia (N. Italy): inorganic geochemistry, fossil pigments and temperature time-series analyses

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ABSTRACT

The palaeoenvironmental history of Lake Candia, a small, shallow, eutrophic lake in Northern Italy, is described for the last ca *2000 years. Sediment samples from a sediment core collected in autumn 1995 were analysed for a range of palaeolimnological indicators, which included the principal algal and sulphur photosynthetic bacterial pigments, as well as magnetic susceptibility, organic matter, carbonates, organic carbon, total nitrogen, total sulphur and various forms of phosphorus. An accurate sediment chronology was determined using ^{210}Pb, ^{137}Cs and ^{14}C. The results show that throughout a first, long phase of the history of this period (from* ca *AD 100 to 1830; zone 1) the sediments have an organic carbon content of* ca *10% d.w. and low concentrations of algal pigments, suggesting a moderately productive environment. Sedimentary carotenoids unique to anaerobic photosynthetic bacteria indicate a seasonally hypolimnetic anoxia during the whole* ca *2000 year period. Clear effects of climate changes on lake productivity were inferred from the carotenoid, ß-carotene, okenone and organic carbon estimates. Values were higher in the warm periods before AD* ca *660 and during the so-called Little Optimum of the Medieval Warm Epoch (AD* ca *1100-1300), and lower during cold moist periods, such as the main phase of the Little Ice Age (AD* ca *1550-1700). After AD* ca *1830 (zone 2), anthropogenic impacts resulted in a sharp increase in lake trophic state, leading first to a decoupling of the trophic state from natural (climate) variability, and then to "cultural" eutrophication. The onset of this latter process in the Turin area has been set around 1830, when a sharp increase of sedimentary sulphur concentration took place.*

Key words: Late Holocene, sediments, nutrients, pigments, time-series analyses, climate change

1. INTRODUCTION

The effects of anthropogenic and natural disturbances on a lacustrine system can be fully appreciated only by knowing the intrinsic variability of the lake during its existence (Likens 1983; Schindler 1987). A number of experiments have shown that many of the otherwise unexplained variations may be due to dynamic food web effects (Schindler 1987; Carpenter & Kitchell 1988). Both chemical and trophic perturbations may induce fluctuations in ecosystem structure that develop over years to decades (Schindler 1987; Carpenter 1988). These variations are difficult to quantify in studies that consider only the recent history of a lake.

Where long-term data on the lake are lacking, palaeolimnological techniques offer a means for reconstructing historical environmental trends from the sediment record. This paper presents results from a high-resolution palaeolimnological study of sediments from Lake Candia (Northern Italy), carried out as part of a comprehensive limnological study to assess the environmental conditions of the lake following restorative measures (see below) (Giussani *et al*. 1997).

Despite more or less continuous seasonal chemical and biological records from 1980 up to the present, no data are available on the original (pre-industrial) condition of the lake. Thus, an important question concerns the extent to which primary production (inferred from plant pigments) and nutrient loading to the lake has changed over time.

The main objectives of the present study were: 1) to make an assessment of changes in the lake during last ca 100 years, including the period of anthropogenic eutrophication; 2) to determine the extent of "natural" variability during the previous *ca* 2000 years, when anthropogenic effects were much lower or negligible; and, 3) to verify the response of Lake Candia sediment to documented climatic changes in Europe, in particular the Medieval Warm Period (MWP) and the Little Ice Age (LIA).

To achieve these objectives, an extensive range of palaeolimnological parameters were considered: magnetic susceptibility, organic matter, carbonates, carbon, nitrogen, sulphur, four forms of phosphorus (apatite-P, inorganic non apatite-P, organic-P and total), and the main algal and anaerobic photosynthetic bacterial fossil pigments.

Since pigment concentrations in lake sediment are often directly related to algal standing stock (Leavitt 1993; Sanger 1988), they can be used to reconstruct phytoplanktonic composition, and to infer total primary productivity and, at times, redox conditions (Züllig 1982; Guilizzoni *et al*. 1983).

Bacterial sulphur photosynthetic pigment populations have also been used to reconstruct the develop-

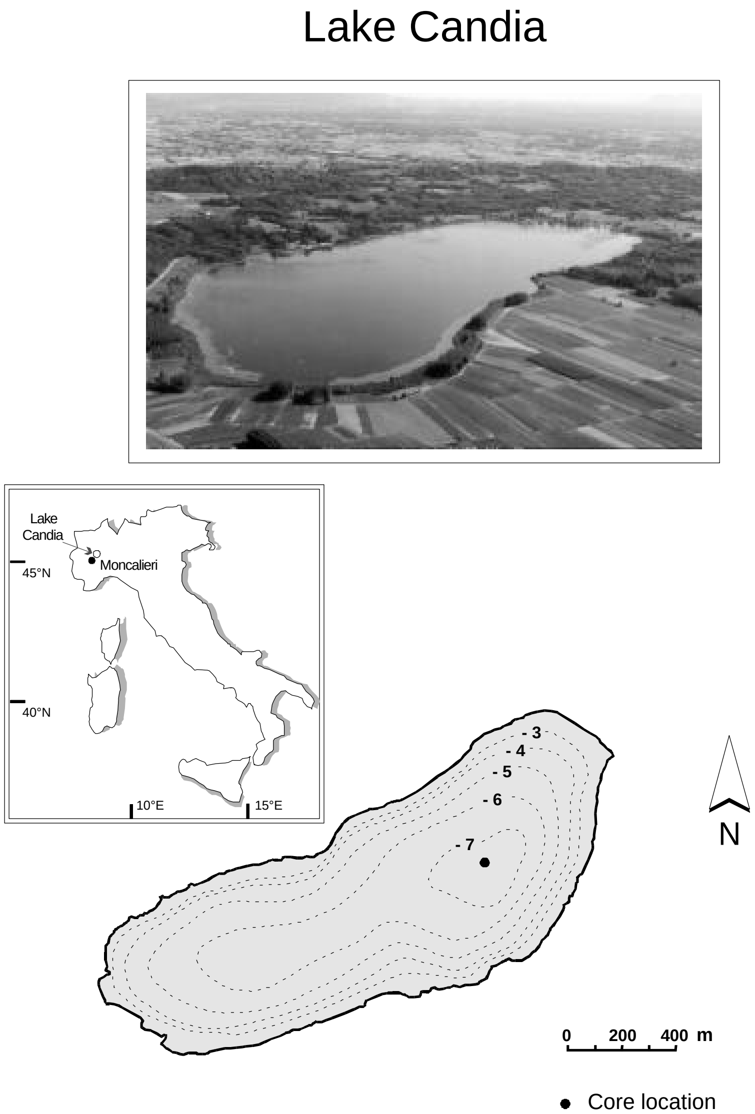

Fig. 1. Photo and map of Lake Candia: the location of core sampling site and of the meteorological station at Moncalieri, near Turin, are also shown.

ment of transparency in the lake and, therefore, its trophic state (Brown *et al*. 1984). In fact anaerobic, green and purple photosynthetic bacteria are common components of meromictic lakes. Since purple sulphur bacteria need higher light intensity than green sulphur bacteria, they stratify near the chemocline. Purple sulphur bacteria contain bacteriochlorophyll-*a* and the carotenoid okenone (Chromatiaceae) or rhodopinal (Rhodospirillaceae), whereas the green sulphur bacteria (Chlorobiaceae) contain bacteriochlorophyll-*a* and the carotenoid isorenieratene. The relative abundance of purple bacteria typically increases under the most eutrophic conditions, when populations of green bacteria, that occupy the deepest strata, almost disappear, because the increase of primary production reduces the penetration of light in the water column.

In strictly anaerobic conditions, *Rhodopseudomonas sphaeroides* produces sphaeroidene while the same purple sulphur bacterium contains sphaeroidenone under low concentrations of oxygen (Züllig 1985); therefore, these two carotenoids typically indicate reducing or mild oxidizing conditions in the lake. The presence of sphaeroidene together with the absence of sphaeroidenone were used by Züllig (1985) to indicate meromixis in shallow lakes.

2. GENERAL FEATURES OF THE STUDY LAKE

Lake Candia (45° 19' 25" N, 7° 54' 43" E) is a small inter-morainic shallow eutrophic lake, located between the cities of Turin and Ivrea (north-western Italy) (Fig. 1). Table 1 gives the main morphometric, physical and chemical characteristics of the lake (Galanti *et al*. 1990; Giussani *et al*. 1997). It receives large nutrient inputs from runoff and from underwater springs. Furthermore, because of its closeness (less than 20 km) to the industrial area of Turin, it also receives heavy loads of sulphur and nitrogen (16 and 17 kg ha^{-1} y^{-1}, respectively in 1986) through atmospheric deposition (Mosello *et al*. 1987).

Tab. 1. Main morphometric, physical and hydrochemical (time-weighed mean values) features of Lake Candia.

Lake surface (km^2)	1.49	Conductivity (μS cm^{-1})	119
Catchment area (km^2)	9.9	pH	7.7
Shore line length (km)	5.7	Alkalinity (meq l^{-1})	0.98
Max depth (m)	7.7	Dissolved O_2 (mg l^{-1})	7.5
Mean depth (m)	3.8	N-NH_4 (μg l^{-1})	185
Max length (km)	2.11	N-NO_3 (μg l^{-1})	92
Max width (km)	0.85	Total Chl (μg l^{-1})	12.4
Lake volume (m^3 10^6)	7.1	Total P (μg l^{-1})	29
Theor. Renew. Time (y)	6.7	P-PO_4 (μg l^{-1})	2.3

Lake Candia is dimictic, presenting a spring (February-April) and an autumn (October-November) circulation. During severe winters, the lake is partially or totally ice-covered from the end of December to mid-February. Secchi disc transparency ranges from 3.6 to 5.6 m.

Analyses of integrated water samples indicate the following biological characteristics:

- Phytoplanktonic population: Chrysophyceae is the dominant group in spring and in autumn; Chlorophyceae, Cryptophyceae and Bacillariophyceae are dominant in summer: some Chrysophyceae and Cryptophyceae develop also in winter.
- Zooplanktonic population: the mains groups are cladocerans (*Daphnia hyalina*, *Ceriodaphnia quadrangula*) and copepods (*Cyclops strenuus*, *Mesocyclops* sp.).

During the summer stratification (May-October), large changes occur in chemical variables, the most important of which is the disappearance of oxygen near the bottom and the increase of nutrients, especially NH_4, in the hypolimnion (Giussani *et al*. 1990; Mosello *et al*., in preparation).

The first limnological investigations of Lake Candia were performed in 1980, when there was a severe reduction of bleak (*Alburnus alburnus alborella*) caused by a pathogenous fungus, *Branchiomyces* sp. (Giussani *et al*. 1980). The bleak mortality was mainly related to lake eutrophication. Measures suggested to assist lake recovery include the diversion of waste waters from littoral recreational and built up areas, the diversion of irrigation waters, and the application of biomanipulation techniques (Kerfoot & Sih 1987; Lampert 1988; de Bernardi & Giussani 1990). In particular, there were attempts to reduce the large population of rudd (*Scardinius erythrophtalmus*), a zooplanktivorous fish, in order to increase the (herbivorous) zooplankton population and so enhance its grazing activity. As there are no important point sources of nutrients, the dominant water chestnut (*Trapa natans* L.) population has been quantitatively harvested in selected seasonal periods (Galanti *et al*. 1990) to reduce internal nutrient loading.

3. MATERIALS AND METHODS

Sediment core sampling. Three sediment cores, CAND 95-1A, 1B, 1C of lengths 97, 106 and 58.5 cm respectively, were collected in autumn 1995 from the deepest point of the lake (Fig. 1) using a gravity corer fitted with a PVC tube 1.5 m long having a diameter of 63.5 mm.

In the laboratory, the cores were cut longitudinally, photographed and their lithological features recorded. They were then sectioned at 0.5 cm intervals between 0-15 cm and at 1 cm intervals below 15 cm (2-47 years resolution). Corresponding slices from the top 15 cm of all three cores were amalgamated to provide sufficient material for analyses. All samples were frozen at -20°C until analysis.

Core chronology. The longer-term chronology was established by AMS ^{14}C dating at the van de Graff Laboratory, University of Utrecht. The analyses were carried out on organic bulk samples from 30, 70 and 110 cm depth in core CAND 95-1B. The recent chronology was established by correlation with an earlier core from Lake Candia (CAND3) collected in July 1990 (Frignani *et al*. 1995) and dated by ^{210}Pb in the Liverpool University Environmental Radioactivity Laboratory, as described below. Bulk sediment accumulation rates (mg dry mass cm^{-2} y^{-1}) were estimated from ^{210}Pb activity profiles and ^{14}C ages.

Water, organic matter and carbonate contents. Water content was determined by drying 5-6 g of wet sediment at a temperature of 80 °C for 48 hours. Organic matter and carbonate content were obtained by the loss-on-ignition (LOI) of dried sediments at 550 °C and 950 °C, respectively (Dean 1974). The dry bulk density of each sediment sample was estimated from water, mineral and organic contents.

Magnetic susceptibility. The magnetic susceptibility of sediments is influenced by their granulometry, and by the ferromagnetic properties of the minerals from which they are formed. Since these minerals derive from the erosion of rocks in the drainage area, measurements of magnetic susceptibility can be used to obtain information about the allochthonous input of sediments to the lake (Thompson *et al*. 1975). This parameter can also be used to correlate the cores, and to provide information on possible disturbances in the sedimentary sequence. Magnetic susceptibility was measured using a Bartington MS IB instrument fitted with a ring sensor having a diameter of 72 mm that is shifted along the core in the two directions at constant velocity.

Carbon, nitrogen and sulphur. Total concentrations of total C, N and S were measured on dry (80 °C) sediment using an "Elemental analyser" (mod. NA 1500, Carlo Erba). Inorganic C was estimated repeating the analyses on the ashes obtained at 550 °C, and organic C was quantified by the difference between total and inorganic C. Results are expressed in percent of the dry weight (%d.w.).

Inorganic, organic and total phosphorus. Three fractions of inorganic phosphorus were quantified using the methods of Hieltijes & Lijklema (1980). The method consists of three sequential extractions: non-apatitic phosphorus loosely absorbed (P-NH_4Cl), was first obtained by suspending 0.3-0.6 g of fresh sediment in 25 ml of NH_4Cl 1M corrected to pH 7 with NaOH. This extraction was repeated twice. The second extraction was performed on the residual sediment with 0.1M NaOH, to determine the concentration of inorganic phosphorus absorbed to metal (Fe, Al) oxides (P-NaOH). The third extraction, performed by 25 ml of 0.5 M HCl, was intended to obtain apatitic phosphorus linked to carbonates and released by the dissolution of oxides. Apatitic P is not potentially available to algae, while P-NH_4Cl and P-NaOH, are considered together as "available P".

Total phosphorus was separately quantified using Vogler's method (1965): 0.05-0.1 g of dry sediment was heated at 550 °C for 8 h and total P was extracted from the residual ash through 20 ml of 1 N H_2SO_4. Following the extractions, phosphorus concentration was measured by spectrophotometry (Murphy & Riley 1962; John 1970). The residual organically bound P was estimated from the difference between total-P and the sum of the above inorganic-P forms. Results are expressed in milligrams per gram of dry sediment (mg $g^{-1}_{d.w.}$).

Algal and bacterial pigments. Algal and bacterial pigments were extracted in 90% acetone, overnight in the dark, under nitrogen. The extract obtained was used both to quantify the chlorophylls and their derivatives (Chlorophyll Derivatives Units, CD, Adams *et al*. 1978) by spectrophotometry (Guilizzoni *et al*. 1982; Züllig 1982), and the individual carotenoids by High Performance Liquid Chromatography (HPLC) using a Beckman System Gold apparatus (Lami *et al*. 1994). Specific extinction coefficients were obtained from Foppen (1971), Davies (1976) and Mantoura & Llewellyn (1983). Pigment concentration were expressed in nanomoles per gram of organic matter (nmol $g_{o.m.}^{-1}$), whereas chlorophyll derivatives were expressed in units per gram of organic matter (U $g_{o.m.}^{-1}$).

Per cent native chlorophyll was obtained spectrophotometrically as the proportion of chlorophyll not degraded to phaeopigments measured through acidification with HCl 0.2M.

Data analysis. Sediment profiles were divided into zones using the Constrained Incremental Sum of Squares (CONISS) procedure, performed on standardised accumulation rates of all measured parameters. The topmost 2-cm zone, consisting of 4 samples, was neglected, considering that very high pigment concentration in the topmost sediment is related to the presence of recent material, which has not yet fully undergone to diagenetic process (Leavitt 1993).

It may be noted that the zonation shown in the biostratigraphic figures (Figs 7-8, 10-13) is obtained on the basis of the standardised accumulation rate of all measured parameters (excluding the topmost 2 centimetres) and then it may not be truly reflected by the parameters shown in each figure.

Temperature time-series. A number of detailed palaeotemperature reconstructions are available from the literature for the last 1000-2000 years for northern hemisphere (Mann *et al*. 1998, 1999) and Europe (Pfister 1984, 1985, 1992; Grove, 1988).

Here we consider three temperature time series obtained from different sources and geographical areas (Fig. 2): (1) the northern hemisphere annual temperature reconstructions, which are based on a proxy-data network for the past millennium (tree rings, ice core $\delta^{18}O$; Mann *et al*. 1998, 1999); (2) Pfister's (1985) Swiss annual average data from 1525 to 1979 based on documentary source materials (e.g., snow-cover, freezing of lakes and rivers, phenophases or other sign of biological activity); and (3) the mean annual temperatures measured at Moncalieri (*ca* 20 km SW of Lake Candia) for the last *ca* 130 years (Biancotti & Mercalli 1987; Di Napoli & Mercalli 1996). The comparison among these long-term temperature series of curves for the overlapping period (after 1865 AD, Fig. 2) shows a high degree of similarity, in particular between the Swiss mean temperature and the Moncalieri record, while the northern hemisphere is smoother.

The generally good agreement between the profile for Moncalieri and both the Swiss annual average and the northern hemisphere annual reconstruction suggests that the latter is suitable for describing climatic trends in the western Po plain. They will then be used to discuss the climatic response of the Candia palaeoenvironmental record prior to AD 1865 (Fig. 2).

4. RESULTS AND DISCUSSION

4.1. Core description

The lithology of core CAND 95-B can be subdivided into four main units (Fig. 3). Apart from the top 8 cm of black fine grained mud (unit 4), the sediment cores were composed of a rather homogeneous brown to light-grey clay (51-74%), silt (26-49%) and sand (>1%) (unit 3-1) (Frignani *et al*. 1995). There was no evidence of annual laminations or turbidite layers.

4.2. Core chronology

The AMS ^{14}C dates for core CAND 95-B are given in table 2. The ^{210}Pb dates for the 1990 core (CAND 3) were relatively unambiguous (Fig. 4). The CRS and CIC models both indicated only minor fluctuations in the sedimentation rate during the past century. They were transferred to CAND 95-B using a linear correlation of the two cores based on magnetic susceptibility (Fig. 3) and the LOI data (not shown). A distinct peak in magnetic susceptibility observed in a number of cores from the lake occurs at *ca* 52 cm in CAND3 and *ca* 39 cm in CAND 95-B (Fig. 3). It is in close proximity to a dis-

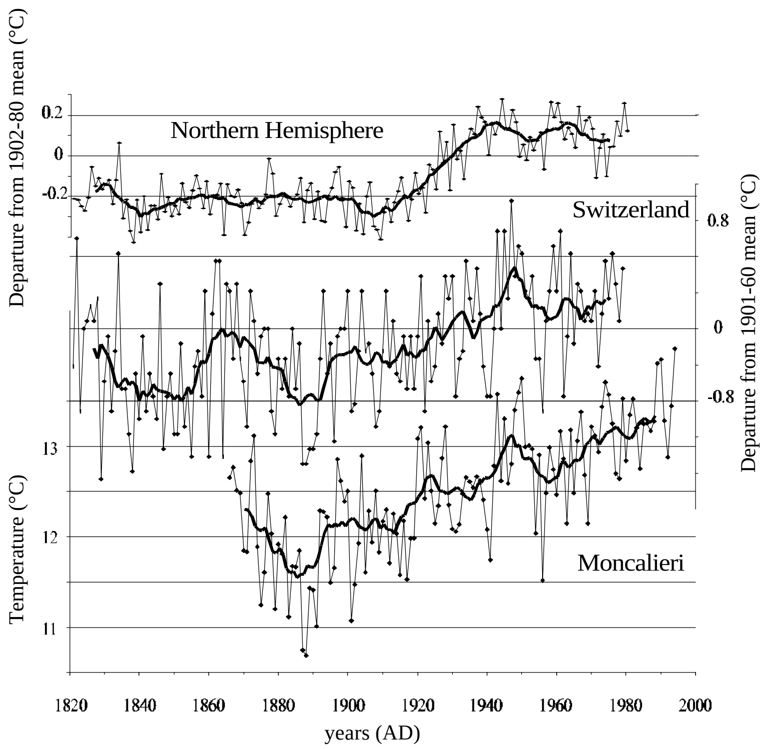

Fig. 2. Comparisons among reconstructed mean annual temperatures for Switzerland (Pfister 1992) and for the Northern Hemisphere (Mann *et al*. 1999), and instrumental mean annual temperatures at Moncalieri, 20 km SW of Lake Candia (Di Napoli & Mercalli 1996), after 1820. 11-year moving averages are also shown.

Tab. 2. Radiocarbon data from the sediment core CAND 95-1B from Lake Candia. Ages are calibrated using the calibration program CALIB 3.0 (Stuiver & Reimer 1993). The error are referred to 1 (one sigma)

Sample depth (cm)	Analysed fraction	Mass (mg)	$\delta^{13}C$ (‰)	Laboratory code	^{14}C Age (y BP)	Calendar Age (y BP)
32	Bulk sediment	2.02	-31.2	UtC7304	425 ± 38	510-470
70	Bulk sediment	2.07	-31.7	UtC7305	790 ± 32	722-669
106	Bulk sediment	2.15	-31.3	UtC7306	1898 ± 39	1874-1808

tinct LOI minimum, at *ca* 55 cm in CAND3 and *ca* 38 cm in CAN-95B (*cf* Frignani *et al*. 1995). The mean depths of these features (53.5 cm in CAND3 and 38.5 cm in CAND 95-B) are thus likely to be more or less contemporaneous. To minimise the effect of sediment compaction, the correlation was calculated using depths measured as cumulative dry mass (in mg cm^{-2}) rather than in cm. Allowance was made for the additional 5 years accumulation in CAND 95-B.

Figure 5 compares the ^{14}C dates for CAND 95-B with the transferred ^{210}Pb dates. The two sets of dates appear to be similar, apart from the anomalous ^{14}C date at 32 cm. The problem of "old carbon" does not appear to a major concern at this site. The ^{14}C dates indicate a sediment rate during the first millennium of *ca* 0.03 cm y^{-1} (7 mg cm^{-2} y^{-1}) compared to more than 0.2 cm y^{-1} (17 mg cm^{-2} y^{-1}) for the modern period. If the ^{14}C dates had been significantly affected by old carbon, matching their true ages with the base of the ^{210}Pb age versus depth curve would imply an earlier and more abrupt transition to these more rapid sedimentation rates, rather than the gradual change suggested in figure 5. Since dramatic changes are more likely to have occurred during the past one hundred years than in the previous centuries, on balance it appears that the older ^{14}C dates are reliable.

Thus, a record of depths and sedimentation rates versus time was calculated using a polynomial fit to the ^{210}Pb and ^{14}C dates (excluding the anomalous value). The results, shown in figure 5, indicate a mean dry mass accumulation rate during the past 100 years of 17 mg cm^{-2} y^{-1} (compared to 22 mg cm^{-2} y^{-1} in CAND 3), more than twice the value near the base of the core of *ca* 7 mg cm^{-2} y^{-1}. The much larger change in volumetric sedimentation rates, from *ca* 0.3 mm y^{-1} at the core bottom to *ca* 3 mm y^{-1} at the surface, reflect the additional effect of a more than four-fold change in dry bulk density.

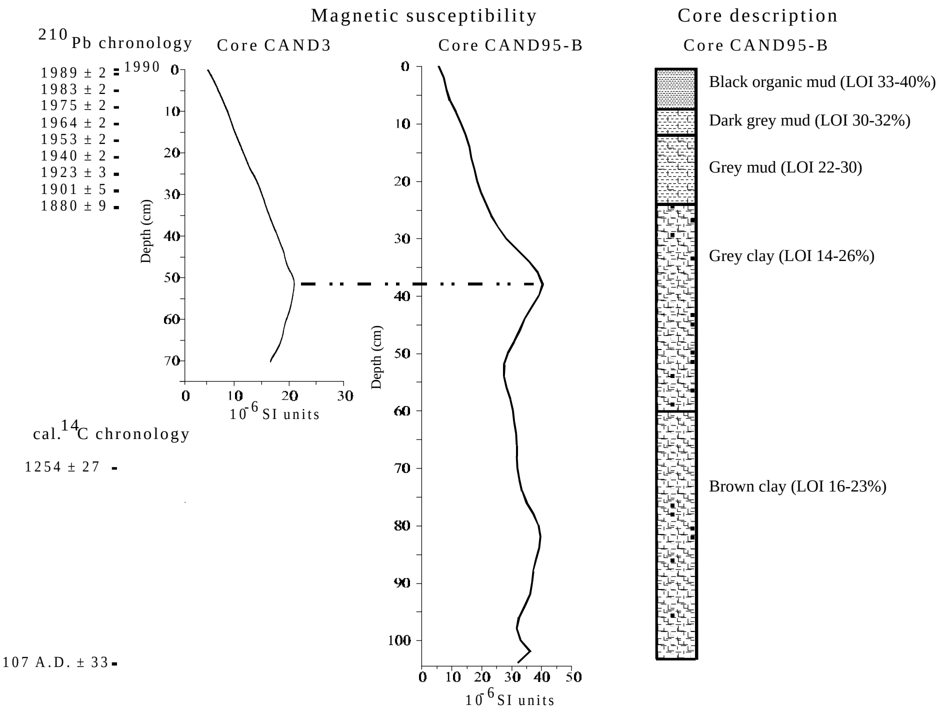

Fig. 3. Core correlation in Lake Candia between the 1990 core CAND3 and the 1995 core CAND95-B on the basis of magnetic susceptibility scans. A broken line has been drawn between the main peak present in both cores. Cores are plotted to match this peak. CAND3 was dated by ^{210}Pb. AMS ^{14}C dates are from core CAND95-B (present study). The lithology of core CAND95-B is also shown.

4.3. Magnetic susceptibility

Before amalgamating samples from the upper 15 cm of each core, it was essential to verify that the cores were sedimentologically identical. Magnetic susceptibility scans have proved to be a useful tool for this purpose. Figure 6 shows the susceptibility data for all three cores. From the similarity of the records, it was possible to obtain an excellent correlation between the cores.

Two periods of high magnetic susceptibility values were detected between 87 and 75 cm (*ca* AD 800 and 1150) and between 41 and 33 cm (*ca* AD 1690 and 1800), indicating high magnetic mineral concentrations in the sediment, likely due to of increased erosion of the catchment. Above 33 cm (after *ca* 1800), there is a progressive decrease of magnetic susceptibility values, coinciding with the strong increase in organic content (see below).

4.4. Water content, organic matter, carbon, nitrogen and sulphur

Percent dry weight values are relatively uniform from the base of the core up to 38 cm (*ca* AD 1770), fluctuating around 20% (Fig. 7). Above this depth they steadily decline to values less than 10% in the surface sediments.

The organic matter varies in an opposite way to the percent dry weight, increasing steadily in the upper part of the core from a minimum value of 12% d.w. at 38 cm to 37% dw in the topmost sediment. Minima at 38 cm and 83 cm may reflect dilution by mineral matter. The $CaCO_3$ contents are negligible, being lower than 2% d.w. throughout the whole core. Organic carbon and total nitrogen trends are similar and present a considerable increase in the upper 30 cm of sediment (from *ca* 1830 onwards), when, in contrast, phosphorus dramatically decreases (see below). As for LOI, slight increase of organic C and total N took place from 60 to 45 cm (*ca* AD 1430-1623) and from 99 to 94 cm (*ca* AD 377-562). The C:N ratio shows values around 10 throughout the whole core suggesting a predominantly autochthonous supply of organic matter (Slack 1954; Hansen 1959a, 1959b; Stefanini 1969; Wetzel 1975).

From the core bottom to the sediment layer corresponding to 32 cm (around 1820 AD), the total sulphur values are stable and lower than 0.5% d.w. After this date, the S content increases up to around 2% dw at 8 cm (*ca* 1980 AD) and then it decreases to about 1% d.w.

Sulphur concentration in the older sediment (zone 1, see Fig. 7) mainly depends on mineralisation of organic matter producing organic S, such as amino-acids and ester sulphate, and reduction of $SO_4^{=}$ to $S^{=}$, caused by oxygen depletion in bottom water and in the sediment (Mitchell *et al*. 1990).

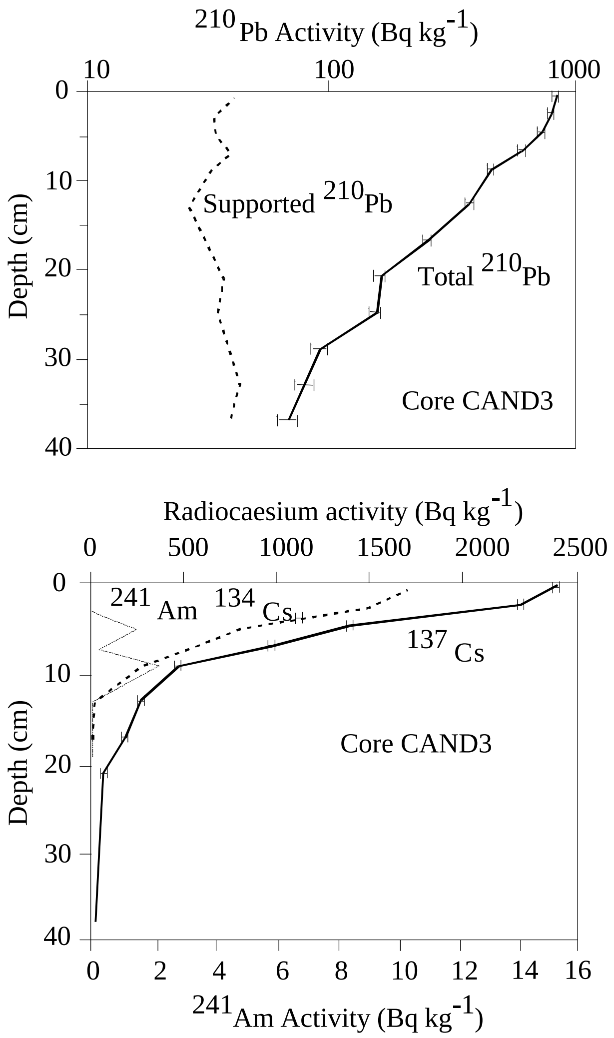

Fig. 4. Profiles of total and supported ^{210}Pb (above), ^{137}Cs, ^{134}Cs and ^{241}Am (below) for the CAND3 core collected in 1990.

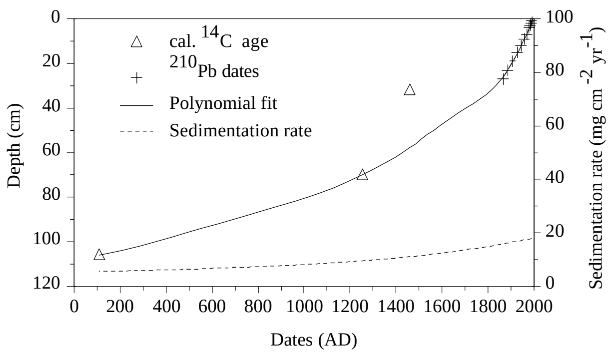

Fig. 5. Age-depth relationship and sediment accumulation rates in the CAND 95-B core.

On the other hand, the sharp increase in sulphur concentration after *ca* 1820 (zone 2) is likely related to increased availability of sulphate because of the high atmospheric deposition of sulphur. Heavy emission of sulphur dioxide into the atmosphere by foundries, metallurgic factories and thermoelectric power stations in the nearby cities of Turin and Ivrea and surrounding region, as well as the heating systems in the towns themselves, has led to high level of sulphate deposition (e.g., Mosello *et al*. 1987; Mosello & Marchetto 1996). For the whole period, most of sulphate carried by atmospheric deposition was trapped in sediment after either its reduction to $S^{=}$ and/or the production of amino-acids and ester sulphates.

The gradual decrease of total sulphur from *ca* 1985 can be explained by both lake restoration measures undertaken from 1986 which improved oxygen level in the lake and the decrease of sulphur load. In fact, the replacement of gas oil by methane in heating systems and the 30%-reduction in S emission between 1980 and 1993 following to the First Sulphur Protocol signed in the framework of the UN-ECE Convention on Long-Range Transboundary Air Pollution reduced emissions in the Po Plain.

In close analogy to sulphur, nitrogen deposition may have contributed to the three-fold increase in N content from 1820 to 1989. Since then, there has been a small reduction, presumably due to the adoption of mitigation measures specifically intended to reduce N emissions following the signing of the First NO_x Protocol in 1988. Using the data for all core sections, there is a strong and significant correlation among N, S and organic C content of the sediment.

4.5. Phosphorus

As for many lakes of the Po Plain (Guilizzoni *et al*. 1983), the remarkable increases of both organic matter and nutrient concentrations in the last two centuries and particularly during the last 50 years are mainly associated with a progressive increase in lake eutrophication. The impact from recreational activities in the 1970s and '80s, and increased runoff from the cultivated catchment, led to the increase in organic matter which parallel the increase in phosphorus concentrations (Fig. 8).

In zone 1, from core bottom to about 32 cm (*ca* AD 133-1825), total phosphorus (mainly as apatitic P) range between 1 and 5 mg g dw^{-1} with high variability. The pattern of P-NaOH (i.e., the inorganic phosphorus adsorbed to metal oxides) is particularly evident. High values of P-NaOH are expected when the redox potential shows positive values and Fe^{+++} and Al^{+++} form insoluble P compounds. A negative relation in fact exists between this "available" P form and the okenone content (*cf* Figs 8 and 12).

The content of P-NaOH is lower in zone 1a (below 91 cm, *ca* AD 133-660) and 1c (61-76 cm, *ca* AD 1125-1429), corresponding to generally known warm periods,

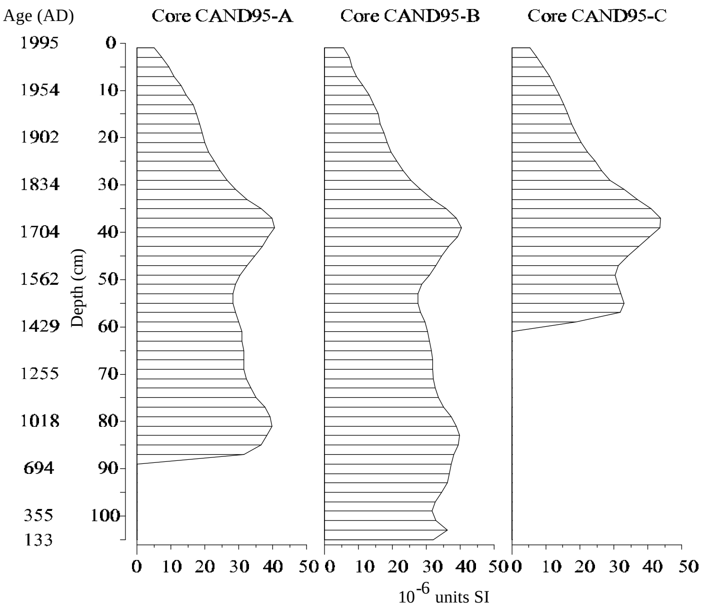

Fig. 6. Correlation of the 1995 cores for Lake Candia based on the magnetic susceptibility scans.

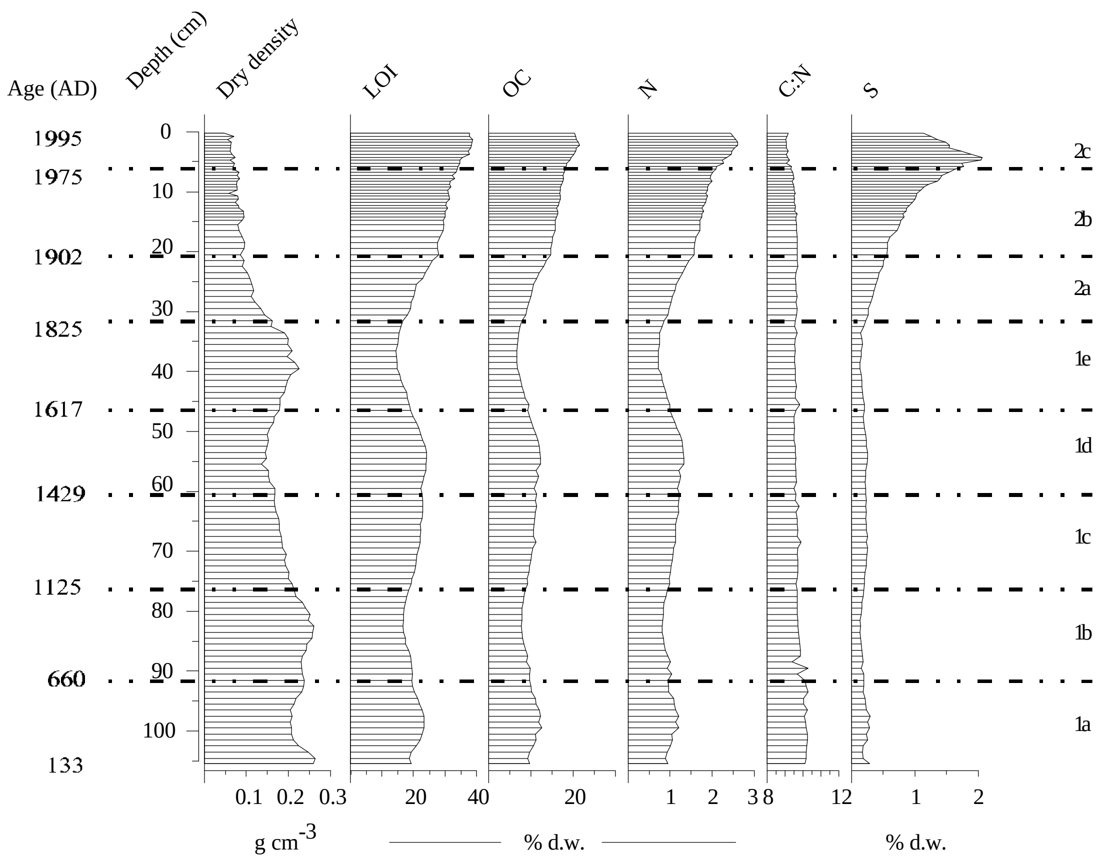

Fig. 7. Lake Candia CAND95-B core. Dry density and some geochemical profiles. LOI = Loss on Ignition; OC = organic carbon; N = nitrogen; S = sulphur. Zones are obtained by constrained incremental sum of square on standardised accumulation rates of all measured parameters.

the first recorded by a general retreat of Alpine glaciers (Pinna 1991), and the later known as the Warm Medieval Period (MWP). In contrast, high P-NaOH levels characterise zone 1b (76-91 cm, *ca* AD 660-1125) and zones 1d and 1e (32-61 cm, *ca* 1429-1825), which together comprise the Little Ice Age (LIA) as defined by Gates (1993).

The good agreement among P-NaOH and total P profiles and climatic variability is driven by increased primary production in warmer years, leading to a lowering of oxygen levels in the hypolimnion and at the water-sediment interface. Evidence of both processes are also shown by pigment profiles, which are discussed later. However they combine to amplify the effect of climate variability on lake primary production, as an increase in the latter would imply more anoxic conditions, leading to P release from the sediment and further increases in primary production.

In zone 2a, 2b and part of 2c (from cm 21 to 4, *ca* AD 1896-1986), all forms of P abruptly decrease and bio-available phosphorus even disappears from sediments for a long period. This pattern suggests a considerable lowering of the redox potential. It may have been driven by an increase in algal biomass due to increasing nutrient levels (see for example N profile in Fig. 7) and consequent increased mineralisation of organic matter

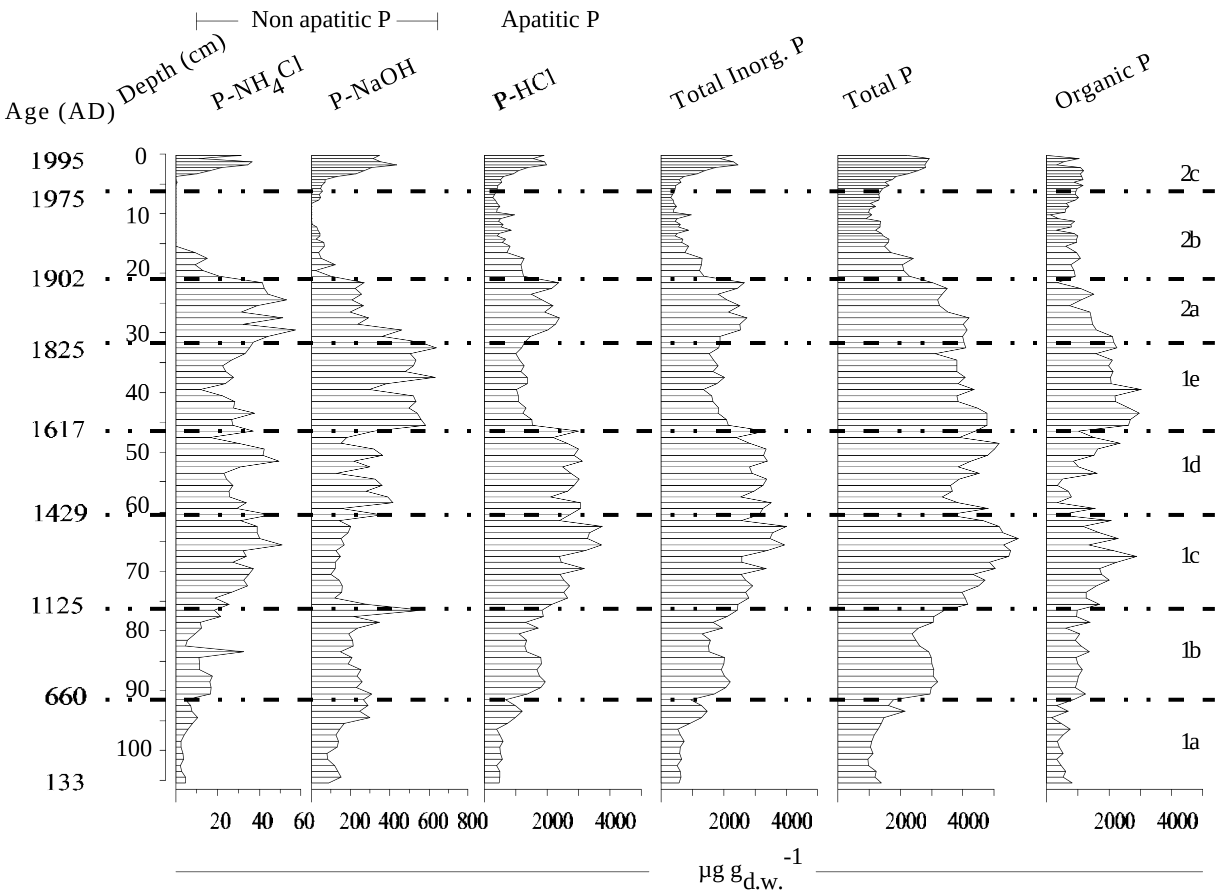

Fig. 8. Lake Candia CAND95-B core. Profiles of apatitic and non-apatitic phosphorus, total inorganic, organic and total P. Zones are obtained by constrained incremental sum of squares on standardised accumulation rates of all measured parameters.

concentration in the lake. However, a strong lowering of redox potential may also be due to an increased rate of sulphate reduction, because of the dramatic increase in S availability caused by its high atmospheric deposition.

Whatever the cause, the disappearance of oxygen at the interface between lake water and sediment caused the release of non-apatitic phosphorus from the sediment.

Despite the strong decreasing trend in P in zone 2a and 2b, a significant inverse correlation with temperature reconstructions and instrumental T time series is found (Fig. 9), i.e. concentration and accumulation rates of total P profile peaks in the colder periods.

Above *ca* 4 cm (AD 1985-1995) all inorganic phosphorus fractions increased, indicating higher redox po-

The increase of apatitic phosphorus between 76 and 46 cm (*ca* AD 1125-1617) might be due to the intensification of runoff caused by increased precipitation. In general, according to Pfister (1985), the remarkable glacial expansion during the LIA in all North-Western Europe was driven by abundant winter rainfalls. Furthermore, the first 30 years of the 17th century were reported to be marked by abundant summer precipitation (Pfister 1985). Therefore, it may be reasonable, in accordance with the dry density profiles (*cf* Fig. 8), to interpret the high values of apatic P as the result of an higher erosion of catchment soils caused by increased rainfall. Apatitic phosphorus increases may also be due to agricultural development (Cinotto & Paglia 1993) with deforested lands being more sensitive to erosion.

tential. These trends are almost certainly related to the restoration measures undertaken in 1986, which led to a decrease in nutrient loading, a decrease in algal blooms and then an improvement of the oxygen level in deeper waters.

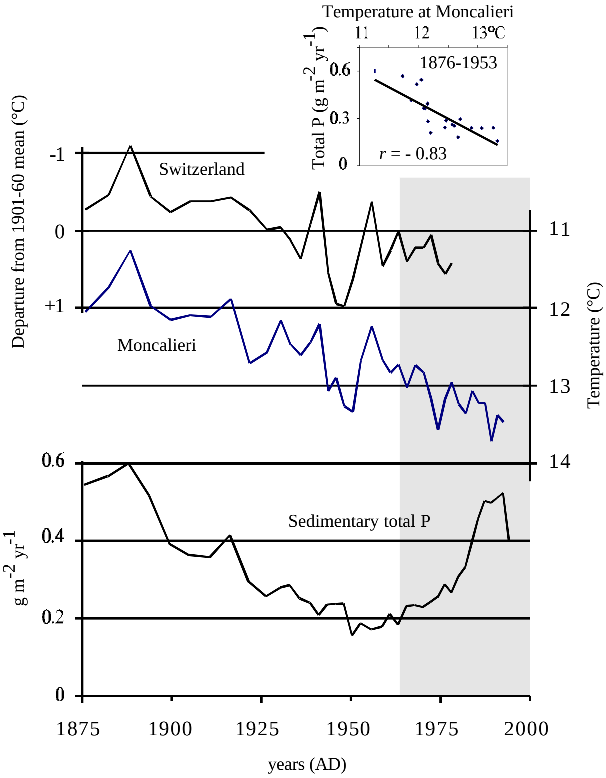

Fig. 9. Comparison of phosphorus concentration in Lake Candia 95-B core with the temperature time-series data, expressed as mean values for each core slice (0.5-1 cm, representing 2-16 years). Departures in temperature from the mean 1901-60 value for the Swiss data are from Pfister (1992) and instrumental records at Moncalieri from Biancotti & Mercalli (1987). The shaded area represents the period after 1953 when the correlation between temperature and phosphorus concentration (shown in the frame) disappears.

4.6. Pigments

In general, with the exception of the bottom 30 cm of the core (zones 1a and 1b, Fig. 10), preservation was good throughout the Lake Candia core. Although phaeophytin-*a* was usually much higher than chlorophyll-*a*, the latter was always present at significant concentrations (Fig. 10). Similarly, labile pigments such as fucoxanthin, chlorophyll-*c* (not shown) and peridinin (Leavitt 1998) were present in all samples. Furthermore, the ratio of 430 nm:410 nm indicates the degree of pigment preservation in the sediments since it is based on the chlorophyll conversion degree to phaeopigments (Guilizzoni *et al*. 1992). The values of this ratio are close to unity throughout most of the core, dropping to *ca* 0.7 in zones 1a and 1b (Fig. 10).

Most pigments reach their maximum level in the topmost 2 cm, where it is almost impossible to single out the contribution of recently settled material. For this reason, these samples will not be further discussed. Chlorophyll-*a* (Fig. 10) is particularly abundant in the uppermost 30 cm of sediment. Total phaeophytin is rather abundant throughout the whole core except in zone 1a (mean value: *ca* 50 nmol $g_{o.m.}^{-1}$), and reaches maximum values in recent times (zone 2, uppermost 32 cm of sediment).

Figure 10 shows the large increase in the concentration of chlorophyll derivatives (CD), and total carotenoids (TC) and total phaeophorbides, which indicate grazing activity, from cm 32 (*ca* AD 1825) to the top of the core. Therefore, lacustrine primary productivity increased during the second half of 19th century and by the 20th century reached values typical of eutrophic lakes. A low CD:TC ratio indicates optimal preservation conditions of pigments in the sediments and low oxygen concentration (Belcher & Fogg 1964; Sanger & Crowl 1979; Swain 1985). The CD:TC ratio is higher in zone 1a and 1b (AD 133-1080), indicating higher oxygen levels, as also shown by the okenone profile (see below).

The stratigraphic sequence of the principal algal and bacterial pigments are as follows (Figs 11-12).

Zone 1a and 1b: 106-76 cm (*ca* AD 133-1125). Algal abundance and/or pigment preservation are low, indicating oligotrophic conditions and high oxygen levels. The higher concentrations in this zone are shown by canthaxanthin and echinenone, typical cyanobacteria pigments, and ß-carotene, produced by both algae and plants (Fig. 12). Lutein, characteristic of Chlorophyta, shows concentration values similar to these former carotenoids (25 nmol $g_{o.m.}^{-1}$). Peridinin, oscillaxanthin and myxoxanthophyll provide minor contributions and almost disappear in the upper sediment layers.

Here we also found low concentrations of okenone and isorenieratene, characteristic carotenoids of purple and green sulphur bacteria respectively. On the contrary, rhodopinal and sphaeroidenone levels are similar to the upper zones, while OH-sphaeroidene is present here at levels around 5-10 nmoles $g_{o.m.}^{-1}$ and virtually disappears at depth of between 70 and 12 cm, confirming high oxygen levels (Fig. 12).

On the whole, the pigment profiles suggest that in a period corresponding to depths of below 76 cm (*ca* AD 133-1125), primary productivity in the lake was rather low, while at depths of between 93 and 80 cm (*ca* AD 500-1000), chlorophyll-*a* and total phaeophorbides concentrations are slightly higher (Fig. 10).

Zone 1c: 76-60 cm (*ca* AD 1125-1429). Among the algal pigments, lutein (mean value: *ca* 70 nmol $g_{o.m.}^{-1}$), canthaxanthin, echinenone (mean value: *ca* 50 nmol $g_{o.m.}^{-1}$) and ß-carotene contents rapidly increase. Also the concentrations of other pigments, such as zeaxanthin, diadinoxanthin and alloxanthin, are higher (about double) than in zone I.

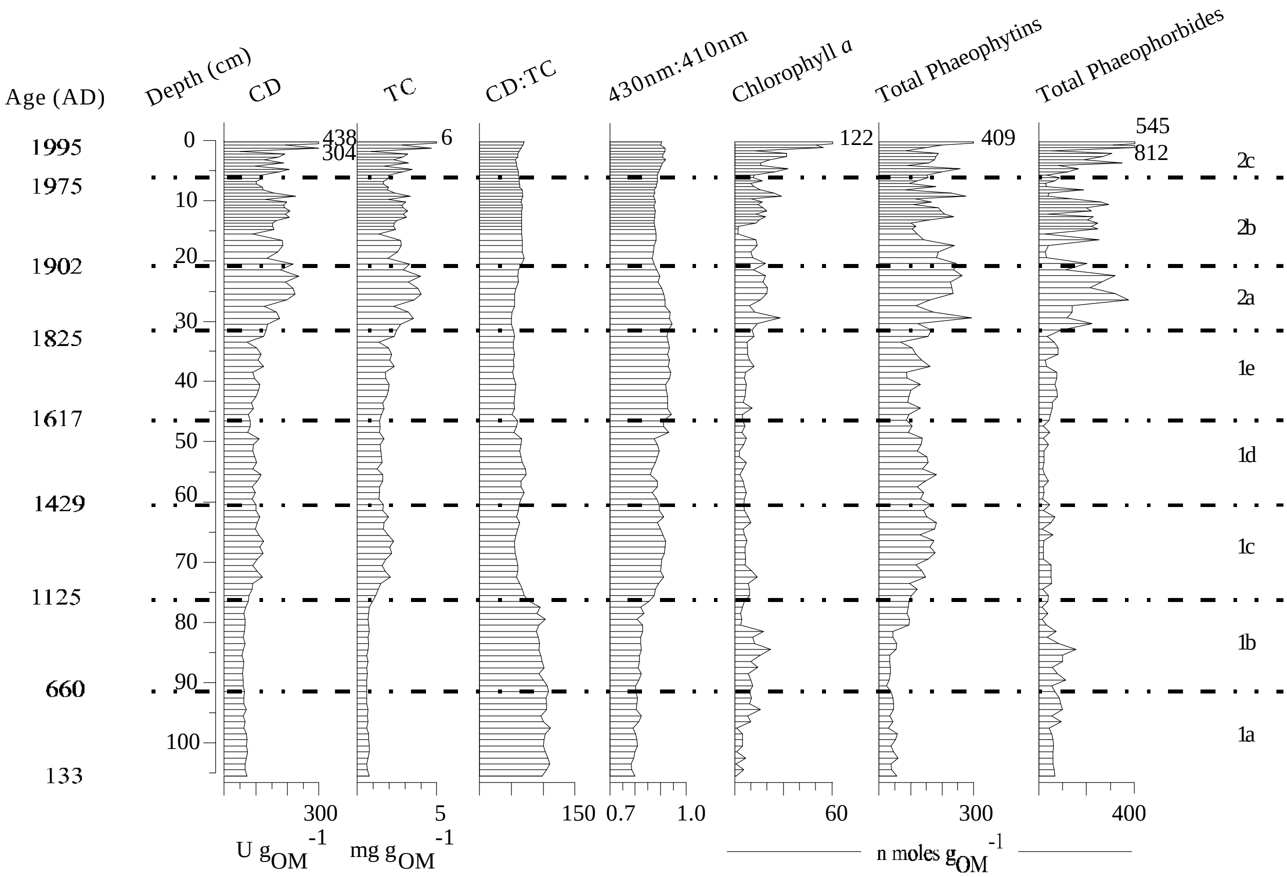

Fig. 10. Lake Candia CAND95-B core. Depth profiles of the concentration of total pigments. Chlorophyll-*a* and the ratio between absorbance at 430 nm and at 410 nm, an index of pigment degradation, is also shown. CD = Chlorophyll derivatives; TC = total carotenoids. U = absorbance units. Zones are obtained by constrained incremental sum of squares on standardised accumulation rates of all measured parameters.

The general increase of almost all pigment concentrations suggests higher primary production, and high levels of echinenone and canthaxanthin indicate the dominance of Cyanobacteria together with Chlorophyta. The increase in primary productivity coincide with the climatic amelioration during the MWP, whose Little Optimum dates around AD 1150-1350 (Lamb 1977). A five-fold increase of okenone content was also found (maximum value: 150 nmol $g_{o.m.}^{-1}$), with high levels of sphaeroidene and sphaeroidenone, while isorenieratene levels compare to the previous zones. These indicate a remarkable lowering of hypolimnetic oxygen level, due to the higher primary production which led to more intense microbial mineralisation, and then to oxygen depletion, allowing the proliferation of the purple anaerobic sulphur bacteria *Chromatium okenii*.

Zone 1d: 60-46 cm (*ca* AD 1429-1617). This zone is characterised by lowering concentrations of lutein, canthaxanthin, okenone and the virtual disappearance of diadinoxanthin, a pigment specific to siliceous algae and Euglenophyta. These trends are probably due to a decrease in primary production, which might be caused by the deteriorating weather characterising the beginning of the LIA. Therefore, oxidising conditions at the bottom of the lake were restored and purple bacteria pigments (okenone and rhodopinal) drastically decrease to levels of around 30 nmol $g_{o.m.}^{-1}$ and below detection limit, respectively.

Zone 1e: 46-32 cm (*ca* AD 1617-1825). In this zone, diadinoxanthin reappears (Fig. 12) suggesting an increasing abundance of Euglenophyta and siliceous algae, such as diatoms and chrysophytes. Lutein, canthaxanthin and astaxanthin also increase, while echinenone and ß-carotene concentration are similar to those recorded in the previous zone. Along zone 1e, rhodopinal reappears and okenone increases, reaching values similar to those found in zone 1c (around 100 nmol $g_{o.m.}^{-1}$), but they both show very low levels in the very last sample of this zone. This pattern is consistent with increasing temperature in the 18th century (*cf* Fig. 13), followed by a short cold pulse between AD 1800 and 1825. Increasing temperature would have led to a new period of high primary production, and lowering of the redox potential in the bottom water, allowing a better development of the anaerobic bacterial community.

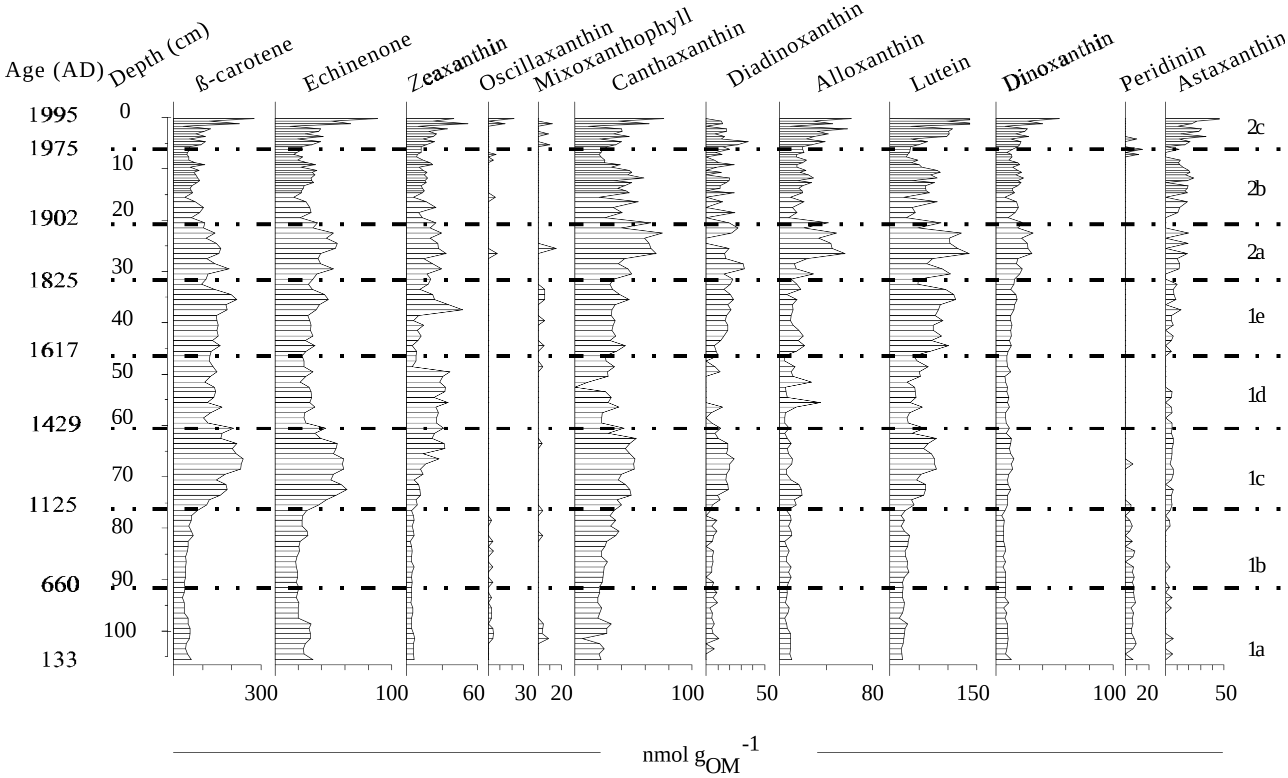

Fig. 11. Lake Candia CAND95-B core. Depth profiles of selected algal carotenoids. Zones are obtained by constrained incremental sum of squares on standardised accumulation rates of all measured parameters.

Zone 2a: 32-21 cm (ca AD 1825-1902). After 1825, all pigment concentrations (Figs 10-12) and accumulation rates increase (Fig. 13). High concentrations of chlorophyll-*a*, phaeophytins and phaeophorbides (Fig. 10) clearly depict the onset of eutrophic conditions in Lake Candia that have lasted until the present. From 1930 onwards industrialisation started in the area (cf. S profile, Fig. 7).

The most evident increase is shown by alloxanthin, indicating a period with high cryptophyte abundance (Fig. 11). However Chlorophyta, cyanobacteria and Dinophyta were also an important component of the algal assemblage, as shown by the increase in lutein, zeaxanthin, echinenone and dinoxanthin concentrations. Okenone, isorenieratene, rhodopinal and sphaeroidene reach their maximum values in zone 2a, indicating lake anoxia. Lowering of the redox potential of lake sediment also led to the dissolution of labile phosphorus compounds stored in the sediment (Fig. 8), allowing a further increase in lake trophic status. It is still questionable if anoxia has been caused by increasing nutrient supply, with consequent increased algal biomass and mineralisation of organic matter, or by the high amount of sulphate available for bacterial reduction.

Zone 2b: 21-7 cm (*ca* AD 1902-1975). Pigment levels in zone 2b are similar to those found in zone 2a, but from 1918 to 1936 isorenieratene totally disappears, and okenone and rhodopinal decrease. Disappearance of green sulphur bacteria and decreases in the abundance of purple bacteria are commonly found during eutrophication of shallow water, due to increasing sulphide levels and decreasing light availability (McIntosh 1983; Züllig 1985).

Zone 2c: 6-2 cm (*ca* AD 1975-1988). In this zone, isorenieratene, okenone and rhodopinal concentrations increase to a level similar to zone 2a, indicating reducing conditions as a consequence of lake eutrophication which, in general, reached a maximum in the 1970s in most sub-alpine lakes. This pattern is in good agreement with the increasing P concentration, as shown in figure 8.

The top two centimetres are not discussed because of the impossibility of quantifying the contribution of recently settled material and/or in-situ growing algae may have made to the high pigment concentration in the very topmost samples.

4.7. Effect of historical climate change on the sedimentary records of Lake Candia

A graphic comparison between the accumulation rates of total phosphorus, C, N, S and some selected algal and bacteria pigments in the sediments of Lake Candia, and the past 1000 years time series data of reconstructed temperatures, shows quite a high coherence of results (Fig. 13). The two most relevant global cli-

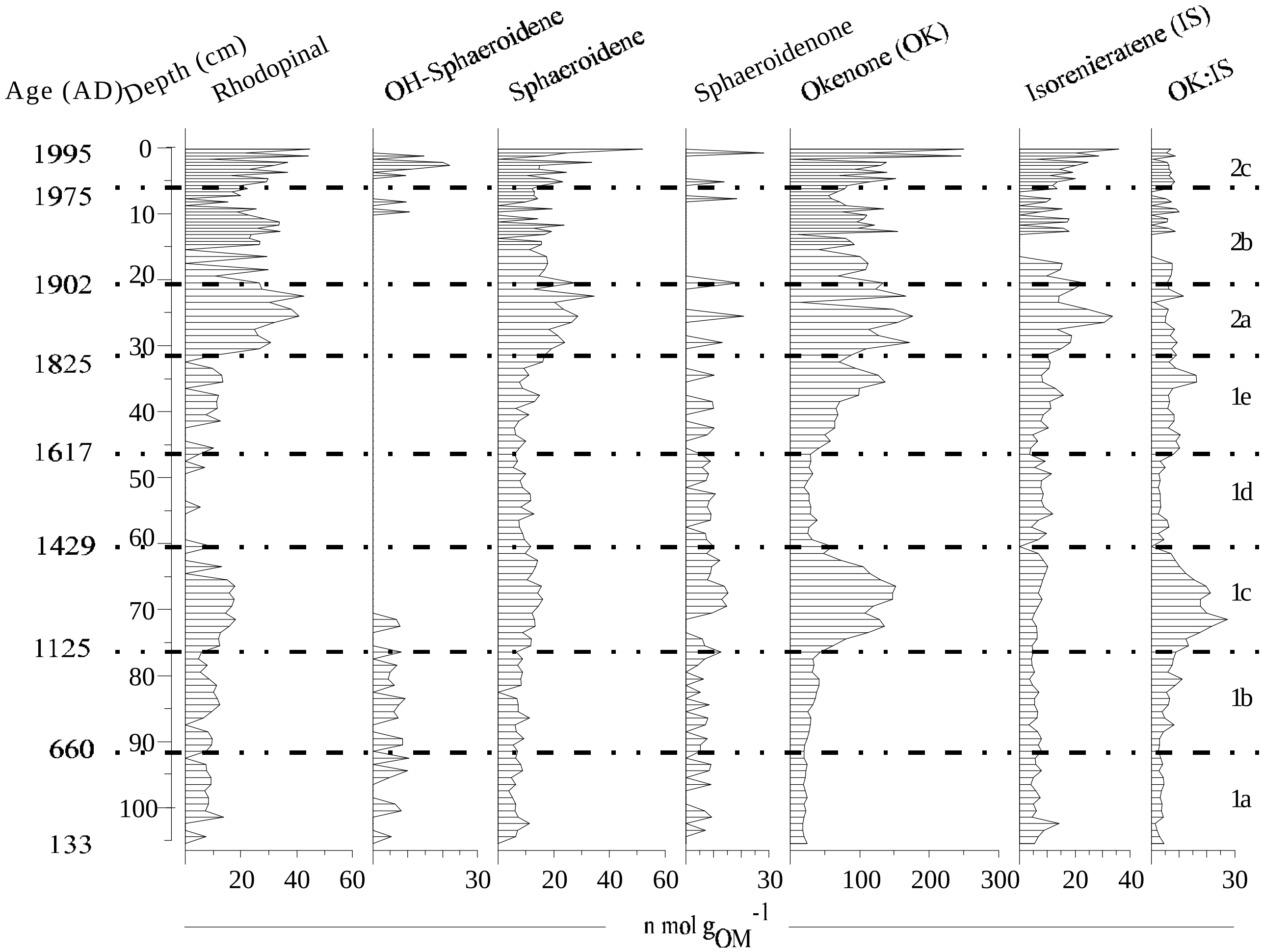

Fig. 12. Lake Candia CAND95-B core. Depth profiles of selected pigments produced by sulphur photosynthetic bacteria. Zones are obtained by constrained incremental sum of squares on standardised accumulation rates of all measured parameters.

mate events, the Medieval Warm Period and the Little Ice Age, as well as other known events (e.g., the glacial retreat), seem to be reflected in the Lake Candia sediments. On the whole, the accumulation rates of pigments increased during the relatively warmer periods, whereas the drop in temperatures and the increase in moisture (*cf* the dry density curve; Fig. 7) during the LIA correlates with a relative minimum in pigment concentrations. Algal biomass, especially the Chlorophyta (lutein) and cyanobacteria (echinenone) (Fig. 11), as well as the purple photosynthetic anaerobic bacteria (e.g., okenone; Fig. 12), all increase during periods of rising temperature. This pattern was amplified by P release from the sediment, driven by the reducing conditions which followed periods of increased primary production. Anoxia in the sediment surface was indicated by high concentrations of pigments from anaerobic bacteria, such as okenone.

Organic carbon and nitrogen show a minimum during the main phase of the LIA: here cyanobacteria seem to be well represented (*cf* also Fig. 11). This could be due to increased inorganic nutrient supply by run-off, as abundant winter rainfalls are considered the driving force of the remarkable glacial expansion during the LIA in all North-Western Europe and the first 30 years of the 17th century were reported to be marked by abundant summer precipitation (Pfister 1985).

Minerogenic input and hence wetter conditions are inferred, in fact, from the peaks of dry density (DD), a proxy-record for erosion and minerogenic input (Ramrath *et al*. 1999). The DD curve shows a detailed record of sedimentary changes and several short-termed periods of high inorganic contribution to the sediments. Three peaks of increased minerogenic allochthonous input are observed, *ca* AD 100, during *ca* AD 900-1000 and the LIA.

After *ca* 1825, the onset of "cultural" lake eutrophication caused a decoupling between pigment concentration and climatic features. However, up until ca 1953, total phosphorus was still related to temperature (*cf* Fig. 9). For the last ca 150 years, during which instrumental temperature data are available and the chronology is reliably determined by ^{210}Pb, we were able to directly compare our sedimentary records with the measured

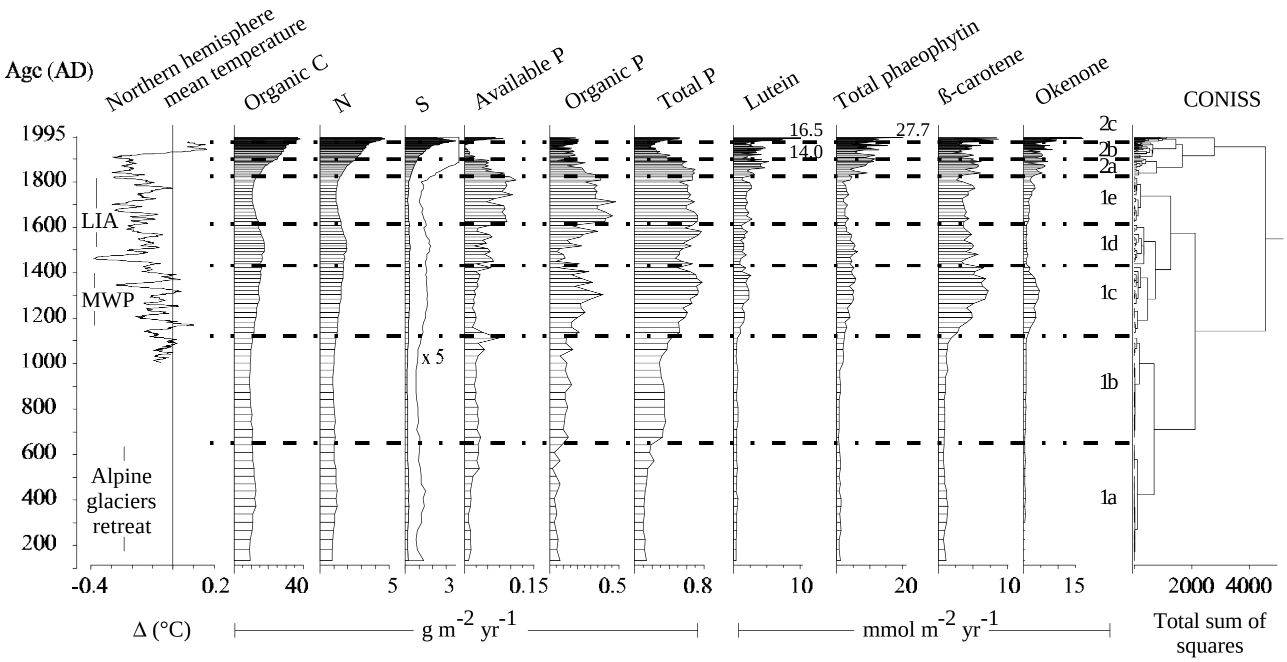

Fig. 13. Lake Candia CAND95-1B core. Summary diagram of selected multi-proxy records for the last ca 2000 years, expressed as accumulation rates. Cluster and zones are obtained by constrained incremental sum of squares on standardised accumulation rates of all measured parameters U = absorbance units. 21-year moving average of the Northern Hemisphere average temperatures during the past millennium (Mann *et al*. 1999) and the period of Alps glacial retreat (Pinna 1991) are also shown.

temperatures. For each core slice, we calculated the average temperature for the period of sediment deposition, and compared this value with the corresponding analysed parameter.

Using the Spearman's rank correlation (p <0.01), a number of significant correlations with air temperature at Moncalieri were found: among these, dry density, sulphur, nitrogen, and organic carbon showed the highest r values. However, these correlations may have been accidental because of the strong increasing gradient of temperature from 1830 to the present day, and perhaps due to the diagenesis of organic matter in the older sediments.

To verify the effect of the increasing temperature trend on our sedimentary records, we investigated if the variables will accurately track the residual, short-term variability of temperature, and repeated the regression analysis using detrended variables. Hence, all correlations between temperature and measured variables disappear, with the notable exception of total P for the period 1825-1953.

As inferred from the abrupt changes in the S and N profiles (*cf* Fig. 13) from *ca* 1830 onwards, atmospheric contributions of such elements as well as local anthropogenic influences on sedimentation, became a major driving force. Indeed, land use in the catchment area (e.g., change in lake hydrology, domestic effluent discharges, biomanipulation techniques in the very recent period), have probably driven these changes and affected lake conditions. These anthropogenic effects are difficult to disentangle from the increasing temperature gradient because no significant differences are noted between the concentration and accumulation rate trends for the last *ca* 150 years. In fact, differences in the two methods of data expression indicate a dilution effect by allochthonous sources, and thus are further indication of human influence (Rein & Negendank 1993).

In summary, over the widest range of climate change, a number of sedimentary records, including some pigment concentrations such as, for example, ß-carotene, phaeophytin and okenone, change in proportion to changes in temperature (Fig. 13). However, over the last *ca* 150 years, strong anthropogenic disturbances may have masked most of the temperature effects.

5. CONCLUSIONS

The present study was undertaken to reconstruct the palaeoenvironmental development of a lake located in the River Po Plain, Lake Candia, during the last *ca* 2000 years. To achieve this objective, several high-resolution geochemical and fossil pigment analyses were performed. The Lake Candia history can be divided into two main periods by a clear change from oligo-mesotrophic to eutrophic condition in the first half of the 19th century.

Before *ca* AD 1825 (zone 1), pigment and nutrient profiles primarily reflect climatic variability, with higher pigment concentration and lower P levels during warmer periods, such as before AD *ca* 660 and during the so-called "Medieval warm period".

In contrast, the post-1825 period (zone 2) is characterised by increasing concentrations of organic matter, total N and S, and algal and bacterial pigments, and evidence of anoxia, primarily related to human impact. After the onset of low redox level at lake bottom, the consequent release of sedimentary P has certainly contributed to the lake trend towards eutrophy. High variability in almost all the measured parameters is evident during the last *ca* 10 years, a period in which restoration measures were undertaken.

Finally, after *ca* 150 years of steadily increasing sulphur concentrations, sulphur declined from the mid-1980s onwards, following atmospheric S reductions.

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