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Chemostratigraphy of late Quaternary sediments from Lake Albano and central Adriatic Sea cores (PALICLAS Project)

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ABSTRACT

This paper summarises the results of the geochemical investigations on bulk sediment and tephra layers from several cores collected, both in Albano and Nemi lakes and in the Middle Adriatic Sea, within the EU funded PALICLAS Project, aimed at the reconstruction of the environmental evolution of central Italy within the last climatic cycle (i.e., the last 30,000 years). The main geochemical effects of the transition from Full Glacial to Holocene times, recorded by lake sediments, are related to changes of organic/inorganic matter ratios, due to different productivity and terrigenous supply; those found the marine sediments reflect the values of some major and trace element, testifying to changes in river supply and marine hydrodynamics. Useful indices for the interpretation of lake palaeoenvironments appeared: total organic content, biogenic silica and Br for biological matter; Al, Y and Zr/Rb ratio for terrigenous clastic material; autigenic U and V/Cr for redox conditions. As regards the Adriatic sediments the more promising geochemical indices of palaeoenvironmental changes in the late Quaternary appeared Cr, Co, Ni, Sr, and Cr/V, Sr/Ca. The occurrence of tephra layers interbedded in both lake and sea samples allowed us the determination of some chronostratigraphic markers for lake-lake, marine-lake and within Adriatic core correlations.

Key words: palaeoenvironment, chemostratigraphy, tephrochronology, Lake Albano, Adriatic Sea

1. INTRODUCTION

The interaction among atmosphere, hydrosphere and biosphere governs the sedimentary processes on the earth crust, so the change and evolution of some environmental parameter can be recorded by variations of physical and chemical properties of sediments. Marine and lake sediment cores provide good records for palaeoenvironmental reconstructions, and within the framework of a multidisciplinary approach, mineralogy and geochemistry can play an important role. Mineralogic and geochemical features of sediments reflect the evolution of the basin area, in most cases controlled by climatic variations, recording changes in erosional and transportational processes, in weathering rates, in biological productivity and in early diagenetic reactions. The size of the catchment area is a fundamental parameter to consider for the correct interpretation of palaeoenvironmental changes; the larger the area (e.g., sea basin) the more complex the system and the variables involved. In small basins (e.g., lakes) the ecology of the system may be strongly influenced by sudden and brief events such as landslides and volcanic episodes. The occurrence of thepra layers interbedded in the sediments allows time controls and may provide markers for core correlations.

Within the EU funded Palaeoenvironmental Analysis of Italian crater lake and Adriatic sediments (PALICLAS) Project, aimed at the reconstruction of the environmental evolution of central Italy within the last climatic cycle (i.e., the last 30,000 years) through physical, geochemical and biological studies of sediments from crater lakes and from adjoining the Adriatic Sea, several cores were collected both in Albano and Nemi Lakes and in the Middle Adriatic Sea. Details on the coring area, location and lithostratigraphical features of each core are reported in Chondrogianni *et al*. (1996, this volume) and in Trincardi *et al*. (1996, this volume) for lake and marine sites respectively.

In this paper the results of mineralogic and geochemical investigations on bulk sediments are summarised, along with those of tephrochronology, based on the characterisation of the volcaniclastic material occurring as tephra layers both in lake and sea cores. The significance of the geochemical variations recorded is discussed in relation to the palaeoenvironmental changes occurred in central Italy during the Late Quaternary, and several tephra beds are pointed out as useful markers for chronostratigraphic correlations among lake and marine cores.

2. CORES DESCRIPTION AND METHODS

Three Adriatic cores (PAL 94/9, PAL 94/8 and PAL 94/66), located along a transect including the continental shelf, the western margin and the deepest part of the Meso-Adriatic Depression (MAD), and one lacustrine core (PALB 94/1E) from Lake Albano, have been extensively analysed (sediment and tephra); only selected samples, representing peculiar layers, were analysed from other Adriatic and lake cores (Fig. 1).

2.1. Adriatic cores

Core PAL94/9, collected west of MAD on the continental shelf at 104 m water depth, is 678 cm long. Sediment is mainly composed of homogeneous mud, but silty laminae occur in the lower part of the core and near the bottom silty mud and sand prevail; a sharp erosional contact divides this coarse sediment from the underlying mud. On the whole this core represents very a expanded record of late Quaternary high stand, and previous sediments are very condensed or missing.

Core PAL94/8, collected from the western margin of the MAD at 150 m in depth, is 500 cm long, and is formed by fine grained sediments (mud and silty mud) with silty laminae relatively sparse and three tephra layers. This core provides an expanded record of the late Quaternary high-stand, but can be condensed during periods of relative rise.

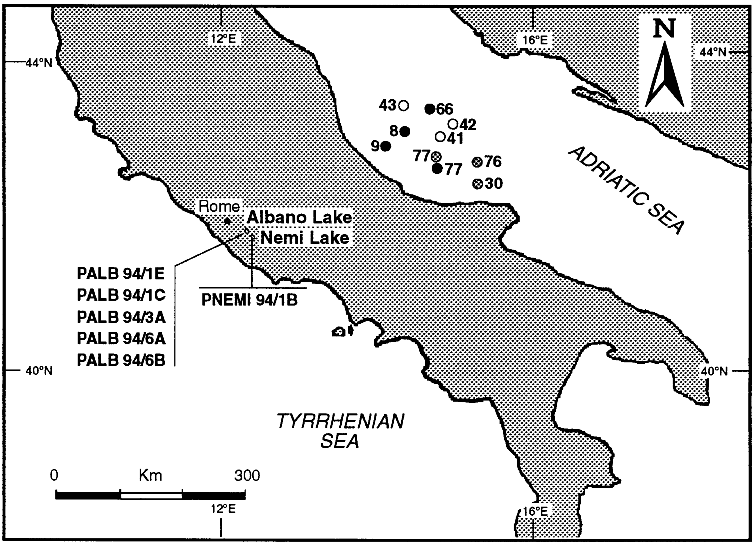

Fig. 1. Locations of the analysed cores from Albano and Nemi lakes and from central Adriatic Sea. Symbols for Adriatic sea cores: open circle, CM92 cores; full circle, PAL94 cores; dotted circle, RF93 cores.

Core PAL94/66, collected at 214 m in the deepest part of the MAD, is 594 cm long and displays general sedimentary features similar to those of PAL 94/8. Laminated sections occur in the upper, middle and lower portions of the core and are particularly well developed in the lower one; four tephra layers stand out in the upper 400 cm. This core provides an expanded section for the early portion of the late Quaternary relative sea level rise, but a more condensed record for the following rise and high-stand.

Sixty-one samples from PAL 94/8 core and eighty from PAL 94/66 core were collected every 10 cm; forty samples were collected from PAL94/9 core, every 15 cm in the lower 400 cm, but every 30 cm in the upper part of the core, owing to sediment homogeneity. Higher resolution sampling (1-2 cm) was made in the core sections where magnetic measurements (Rolph *et al.* 1996, this volume; Alvisi & Vigliotti 1996, this volume) suggested the occurrence of tephra layers. The analyses were carried out on samples washed with deionized water to remove sea salts.

2.2. Lake cores

Core PALB94/1E, collected at 70 m water depth inside Lake Albano, is about 1400 cm long, and consists of grey silts and mud. The sediment is rich in organic matter in the upper half of the core, and of calcite layers in the lower portion; the bottom of the core is composed of coarse (centimetres) volcanic fragments, related to a phase of Alban Hills volcanism dated about 25 kyr BP (I. Villa, pers. comm.), but fine-grained volcaniclastic material, derived from the weathering of catchment rocks, occurs throughout the core. Two tephra layers have been recognised at 354 and 717 cm depth respectively. From the whole of PALB 94/1E 87 samples were collected, one every 25 cm and with closer spacing near chemical boundaries.

2.3. Methods

Each sample was dried at room temperature, weighed and split to obtain about 0.7 g for analyses. This fraction was crushed by hand into an agate mortar and used for X-ray diffractometry (XRD), X-ray fluorescence (XRF) and thermal analyses (TG, DTG, DTA).

Mineral composition has been determined by X-ray diffractometry (Philips PW 1130, Cu K_α radiation, Ni filtered) by pressing powders into alumina holders, to prevent strong orientation of sheet-silicates. Chemical analyses of major and trace elements were made on powder pellets by X-ray fluorescence (Philips PW1480, Rh tube) applying a full matrix correction procedure (Franzini *et al*. 1972, 1975; Leoni & Saitta 1976; Leoni *et al*. 1982). Thermal analyses, performed only on the lake samples to distinguish and evaluate mainly H_2O, organic matter and CO_2, were carried out by Setaram TAG 24 analyser in a temperature range from about 20 to 970 °C, after sample stabilization at room temperature in CO_2 for 10 minutes. On the sea core samples, total loss on ignition (LOI) was gravimetrically estimated after overnight heating at 950 °C.

Tephra analyses were performed both on bulk samples, following the above procedures, and on separated volcanic glass fragments. Major elements were determined on glass shards (grain size >63 µm) mounted on epoxide resin, using a Philips 515 scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDAX 9100). To minimise the sodium loss, the beam was scanned over the sample during the scan time (100s) and correction was applied following suggestions of Calanchi *et al*. (1994).

3. RESULTS

3.1 Adriatic cores: mineralogy and geochemistry

The main mineral phases in the Adriatic sea sediments are: quartz, calcite, dolomite, feldspars, micas, clay minerals (muscovite-illite, smectite and chlorite) with occasional occurrences of amphiboles and serpentine. The comparison of XRD patterns suggests regular downward increase of dolomite coupled to regular decrease of calcite and quartz; in core PAL 94/8 these last phases display a moderate increase in the lower part (below 360 cm). Feldspars are enriched in the sediment where lie the tephra layers, and higher frequency of amphibole and serpentine is observed in the upper portion of the cores.

The bulk geochemistry of the cores (Tab. 1) is consistent with the average composition of fine-grained Middle Adriatic sediments, and major variations depend on changes in the silicate/carbonate ratios, and in the type and abundance of silicate supply. Element depth profiles from cores PAL 94/8 and PAL 94/66, those that record also pre-Holocene sediments (Figs 2-3), point out clear chemical zoning, and allow us to group the elements as follows:

Tab. 1. Ranges of bulk sediment composition of Adriatic Sea cores and geochemistry of selected layers from Lake Albano cores. Identification number of Lake Albano core samples corresponds to depth in cm from the top of the core.* For Lake Albano samples: LOI <650 °C (organic matter). n.d.: not detected; ---: not analyzed. Sibio nor: normalized biogenic silica (%) according to Robinson *et al*. (1993). For Aut. U (autigenic U in ppm) see Jones & Manning (1994).

	ADRIATIC SEA CORES						**LAKE ALBANO CORES**					
	PAL94/9		PAL94/8		PAL94/66		PALB94/1E				94/3A	94/6B
wt %	range		range		range		1383	1139	788	457	912	821
SiO_2	34.41	47.22	34.04	39.28	33.44	41.76	43.34	27.68	62.96	61.01	58.53	41.87
TiO_2	0.42	0.54	0.45	0.53	0.42	0.79	0.80	0.10	0.49	0.13	0.26	0.63
Al_2O_3	9.22	12.66	10.02	14.10	10.22	14.96	15.31	2.79	11.81	3.07	6.20	15.01
Fe_2O_3	3.19	5.22	3.94	5.02	4.33	6.33	8.06	1.06	4.67	1.16	2.09	5.91
MnO	0.07	0.11	0.07	0.12	0.09	0.43	0.19	0.04	0.07	0.02	0.04	0.11
MgO	4.72	5.73	4.20	6.34	4.63	6.02	5.45	1.24	2.33	0.51	0.89	4.78
CaO	14.73	19.30	13.07	20.25	12.19	19.70	13.08	33.26	3.11	0.98	1.24	15.45
Na_2O	0.49	1.12	0.62	1.05	0.59	1.48	2.29	0.37	0.37	0.18	0.30	0.80
K_2O	1.39	1.90	1.58	2.48	1.64	2.76	5.99	0.65	2.01	0.48	0.82	4.96
P_2O_5	0.06	0.12	0.06	0.12	0.06	0.21	0.86	0.09	0.34	0.10	0.24	0.41
LOI	16.79	23.18	18.26	25.45	14.52	27.18	*1.11	4.90	6.44	22.97	20.00	2.18
CO_2	---	---	---	---	---	---	2.74	25.88	n.d.	n.d.	n.d.	5.02
S ppm	317	1092	101	558	117	1440	3989	1926	4291	5582	6110	1088
Sc	6	29	15	24	9	25	28	24	6	n.d.	1	21
V	63	125	73	109	87	117	238	63	220	271	586	174
Cr	83	152	87	161	67	204	44	13	23	10	22	57
Co	4	18	8	21	7	26	28	1	16	2	6	20
Ni	45	101	50	127	48	188	39	17	26	7	13	38
Cu	20	38	14	35	3	24	128	45	77	1	n.d.	39
Zn	48	96	51	512	57	211	87	34	66	26	29	48
Ga	10	21	9	25	9	21	22	n.d.	2	n.d.	3	11
As	n.d.	12	2	33	n.d.	30	4	6	40	46	52	12
Br	---	---	---	---	---	---	n.d.	29	40	208	281	n.d.
Rb	64	134	88	152	83	159	353	58	248	43	89	454
Sr	216	492	226	620	179	596	2291	1630	2770	326	539	2096
Y	14	27	19	31	15	29	40	7	25	8	14	28
Zr	55	160	86	137	66	194	340	46	191	58	106	254
Nb	6	12	8	16	5	34	29	5	19	4	9	13
Mo	---	---	---	---	---	---	4	n.d.	3	6	9	1
Ba	245	313	195	473	182	614	1158	300	867	277	650	1454
La	19	38	21	39	20	59	109	29	85	25	51	73
Ce	35	69	38	69	37	110	213	59	168	49	85	122
Pb	11	24	4	101	13	60	47	3	55	8	28	39
Th	1	11	4	14	n.d.	18	51	7	35	8	18	28
U	---	---	---	---	---	---	10	7	12	31	27	n.d.
Sibio nor	---	---	---	---	---	---	0.5	19.9	29.9	52.4	41.2	n.d.
Aut. U	---	---	---	---	---	---	n.d.	4.7	0.3	28.0	21.0	n.d.

- group A: Si, Al, Fe, K, Rb, Ba, As, Zn, V and Ga, elements generally associated to the silicate fraction (quartz, plagioclase, illite and micas);
- group B: Ca and loss on ignition (LOI), mostly associated to the carbonate fraction of the sediment;

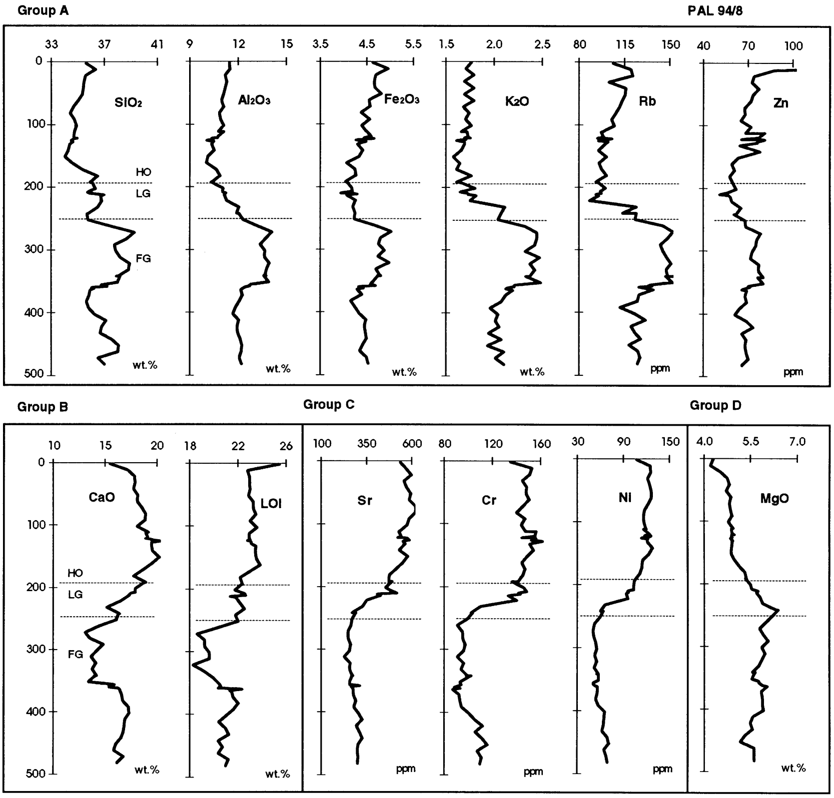

Fig. 2. Core PAL 94/8 - Representative major and trace element depth profiles. Dotted lines represent the limits of Full Glacial (FG), Late Glacial (LG) and Holocene (HO) according to Oldfield (1996, this volume) and Trincardi *et al*. (1996, this volume). Depth scale is in cm.

- group C: Sr, Cr, Co and Ni. Strontium, according to depth profile, represents mainly calcite variations; Cr, Co and Ni seem to be associated to a minor fraction related to mafic and ultramafic source rocks.
- group D: Mg variations can be assumed to represent mostly the changes in dolomite content of the sediment.

Other elements display only irregular peaks and cannot be fitted into any of the above described groups. The spikes, observed in some depth profiles, occurring at about 215 and 360 cm from the top of PAL94/66 core, mark tephra layers (C-1 and Y-1, see below) interbedded within the sedimentary succession.

The above chemical groups can be roughly extended also to core PAL 94/9 (Fig. 4), even if Si behaviour in the lower 2 meters of the core is different from other silicate elements, and the expanded Holocene section leads to more homogeneous sediment composition. It is however important to note the larger silicate/carbonate ratio in this core with respect to the other two, and the persistence of peculiar patterns in Sr, Cr, Co and Ni depth profiles.

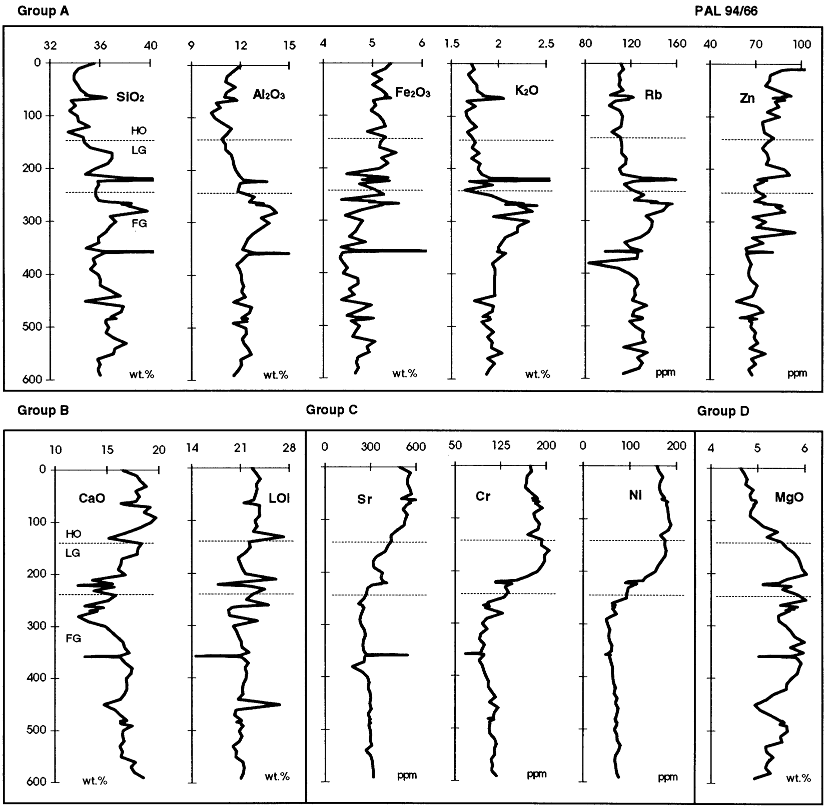

Fig. 3. Core PAL 94/66 - Representative major and trace element depth profiles. Dotted lines mark the limits of Full Glacial (FG), Late Glacial (LG) and Holocene (HO) according to Oldfield (1996, this volume) and Trincardi *et al.* (1996, this volume). The spikes of some elements at 356 cm in depth are related to the presence of Etna Y-1 tephra layer (14.2 kyr BP); the spikes at about 215 cm in depth mark the layer of C-1 Campanian tephra (Pomici principali, 9.8 kyr BP). Depth scale is in cm.

3.2. Lake cores: mineralogy and geochemistry

The minerals identified in lake sediments are typical of the Alban Hills volcanism: leucite, analcite, zeolite, phlogopite, clinopyroxene, olivine and feldspars; in addition calcite and/or amorphous material, mainly silica, occur in several samples. In PALB94/1E core calcite occurs only below 1100 cm and above 150 cm, with two exceptions at 354 and 878 cm; amorphous silica (biogenic) increases above 600 cm and reaches the highest values in the range 500-400 cm. The contents of the remaining phases are in opposition to those of calcite and silica, with high values in the range 1000-600 cm and above 400 cm.

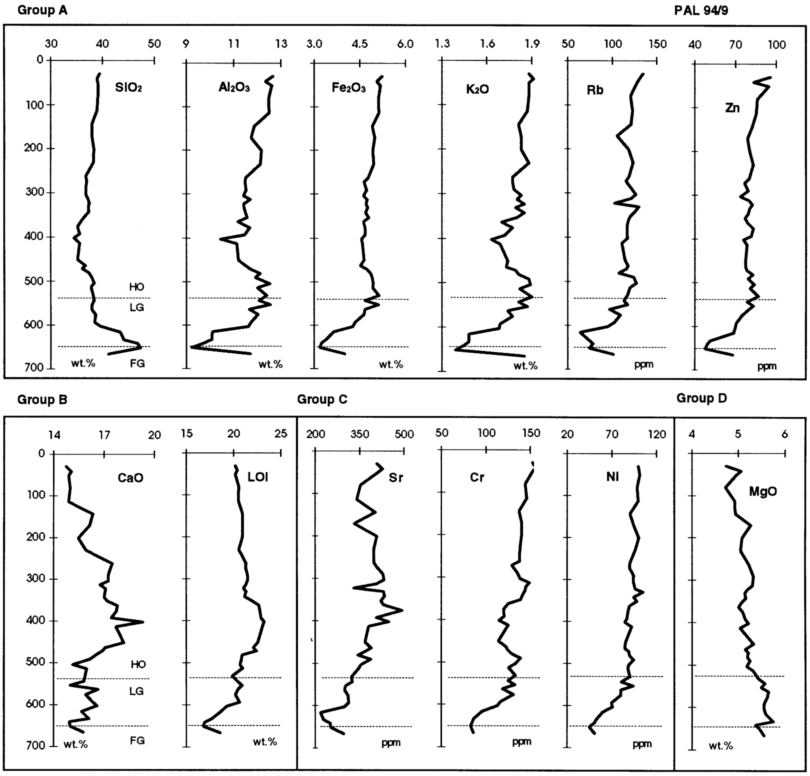

Fig. 4. Core PAL 94/9 - Representative major and trace element depth profiles. Dotted lines mark the limits of Full Glacial (FG), Late Glacial (LG) and Holocene (HO) according to Oldfield (1996, this volume) and Trincardi *et al.* (1996, this volume). Depth scale is in cm.

Although chemical features of the samples reflect their main mineralogic composition, the mark of Alban Hills volcanism is clearly evident in the analysed cores, and the ratios of reworked volcaniclastic vs. biogenic materials gives to the sediment chemistry a wide variability. Chemical analyses and some geochemical indices of selected layers of Lake Albano sediments are in table 1; normative biogenic silica values (Sibio nor= SiO_2-2.8*Al_2O_3; Robinson *et al.* 1993) were calculated to evaluate the diatom productivity; autigenic U (Aut. U= total U-Th/3) values were used as reliable indices of palaeoredox conditions (Jones & Manning 1994). Sample 1383 cm from PALB94/1E core represents the volcanic rock fragments of the bottom, similar to other volcanic products of Alban Hills outcropping on the lake slopes; sample 1139 cm is a carbonate-rich layer; sample 788 cm represents the normal sediment; sample 457 cm is a layer very rich of biogenic matter.

Chemistry of three layers analysed from another core (PALB94/3A) (869 cm, 870 cm, 911 cm) reflects a mixture of reworked materials of Alban Hills composition with a high content of amorphous silica and organic matter. Such features, represented in table 1 by sample 912 cm, agree with those of dark layers found in the 500-400 cm depth range of PALB94/1E (Tab. 1, sample 457 cm, and Fig. 5). The samples from PALB94/6A core (top 2-4 cm, and 623 cm) and PALB94/6B (405, 733, 770, 795, 802, 821 and 832 cm) appear to be mixtures of minerals and rock fragments without glass shards. Chemical analyses reflect the variability of mineral compositions but confirm the affinity to the Alban Hills volcanism (e.g., Tab. 1, core 6B, sample 821 cm).

A more complete picture of the geochemical features of Lake Albano sediments and of their evolution with time results from the extensive sampling of PALB94/1E core, where major and trace elements variations with depth define a chemical zoning based on three main groups of elements (Fig. 5):

- group A: Ti, Al, Fe, Mn, Mg, K, Sc, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb and Th, elements mainly carried by the siliciclastic phases;
- group B: Si, LOI, V, U, As, Br and Mo, elements carried by both siliciclastic phases and organic matter;
- group C: Ca and CO_2, elements mainly carried by the carbonate fraction.

Of the remaining elements, Na and P behaviour is intermediate between the A and B groups, and S displays remarkable fluctuations, though its behaviour is closer to the A group elements.

The spikes of some silicate elements occurring at about 717 cm and 354 cm can be attributed to tephra layers (Etna Y-1 and "Avellino Plinian erutpion", respectively).

3.3. Lake and sea tephra layers

The work on tephra layers was carried out mainly through SEM-EDS analyses on separated glass shards, as bulk sediment analysis only in few cases gave results useful for tephra characterisation. Representative analyses of glass fragments from lake and Adriatic tephra layers are reported in table 2, along with inference of their provenance and age.

The characterisation of tephra was based on the comparison of chemical features (major elements) of analysed samples with those of both land and marine samples from the literature. The criteria followed for provenance and age attributions included also: the presence of a single layer or of sequences of layers; the chemical homogeneity or the compositional variability of glass shards in the layer; the layer depth and its stratigraphic location in the core. These criteria allowed us to distinguish material of different origin, but the correlation with on land products could not always be unambiguously defined, as in some cases of Campanian volcanic episodes (cores RF93/30, 530 cm, and CM92/42, 400 cm). The results of tephra characterisation are summarised in table 3 and figure 6; the main markers so far identified useful for inter-core (chrono) stratigraphic correlations are the following:

- *lake-lake core* correlations: AV "Avellino" (3.7 uncalib. kyr BP) from Somma-Vesuvius.
- *lake-Adriatic core* correlations: Y-1 layer (14.2 uncalib. kyr BP) from Etna volcano.
- *between core Adriatic* correlations: AMS "Agnano-Monte Spina" (4.4 uncalib. kyr BP), C-2 "Yellow Neapolitan Tuff" (12.3 uncalib. kyr BP) and Y-5 "Campanian Ignimbrite" (about 35 uncalib. kyr BP) from Phlegrean Fields; C-20 (about 67 uncalib. kyr BP) from Campanian area.

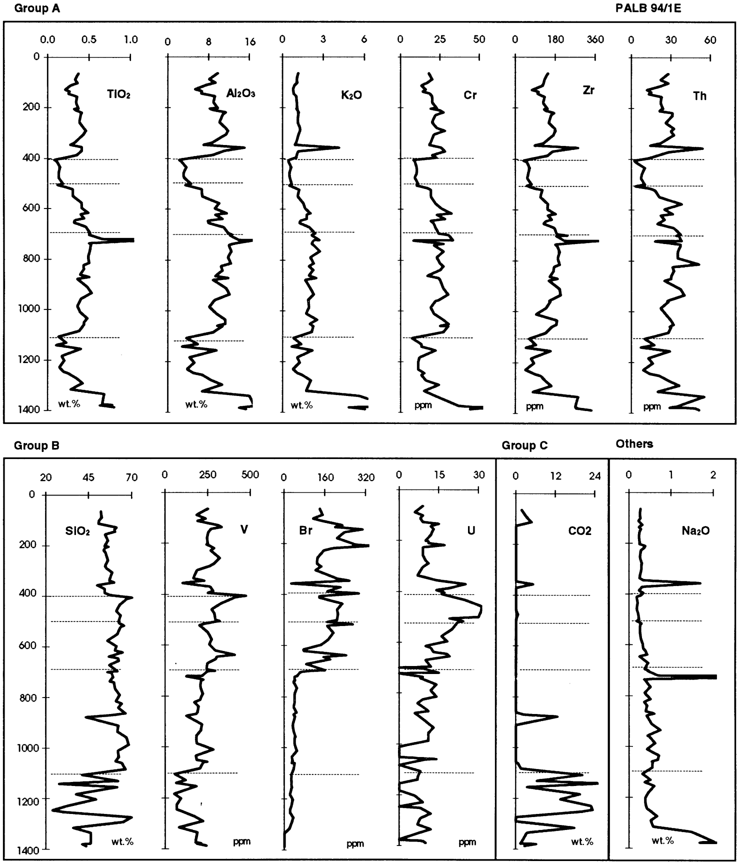

Fig. 5. Core PALB 94/1E - Representative major and trace element depth profiles. Depth scale is in cm. Dotted lines mark the limits of the five chemical zones identified (see text). The spikes at 354 cm are related to a tephra layer from Somma-Vesuvius (Avellino, 3.7 kyr

BP); those at about 717 cm mark Etna Y-1 tephra layer (14.2 kyr BP).

Tab. 2. Representative SEM-EDS analyses of glass shards in tephra layers from Albano (PALB 94/1C) and Nemi (PNEMI 94/1B) lakes and Adriatic Sea cores. For each core are reported the depth in cm from the core top, and in brackets the number of point analyzed; s.d.: standard deviation. Provenance and age of tephras are defined in comparison to literature data: **AV** - "*Avellino* plinian eruption" from the Somma-Vesuvius volcanic center. Correlation based on bulk rock analyses from Santacroce (1987). **AMS** - "*Agnano-Monte Spina* eruption" from the Phlegrean Fields area. Correlation based on bulk rock analyses from Di Girolamo *et al*. (1984) and Rosi & Sbrana (1987). **C-1** - "*Pomici Principali*" / "*Ancient Agnano* plinian eruption" from the Phlegrean Fields area. Correlation based on bulk rock analyses from Di Girolamo *et al*. (1984), Rosi & Sbrana (1987) and on glass-shards data from Paterne *et al*. (1988). **C-2** - "*Neapolitan Yellow Tuff*" from the Phlegrean Fields area. Correlation based on bulk rock analyses from Di Girolamo *et al*. (1984), Rosi & Sbrana (1987), Orsi *et al*. (1992) and on glass-shards data from Paterne *et al*. (1986), Paterne *et al*. (1988), Orsi *et al*. (1992) and Calanchi *et al*. (1994). **Y-1** - "*Biancavilla-Montalto* event" from the Mt Etna. Correlation based on bulk rock analyses from Duncan (1976) and on glass-shards analyses from Paterne *et al*. (1988), Vezzoli (1991), Narcisi (1993), Calanchi *et al*. (1996b). **Y-5** - "*Campanian Ignimbrite*" from the Phlegrean Fields area. Correlation based on bulk rock analyses from Rosi & Sbrana (1987) and on glass-shards data from Paterne *et al*. (1988), and Vezzoli (1991). **C-20** - Unnamed event from the Campanian area, correlation based on glass-shards data from Paterne *et al*. (1988). Ages are not calibrated years.

	AV		AMS		C-1		C-2		Y-1		Y-5		C-20	
	3.7 kyr		4.4 kyr		9.8 kyr		12.3 kyr		14.2 kyr		~ 35 kyr		67.5 kyr	
	PNEMI94 450 (19)		PAL94/66 64 (22)		PAL94/66 214 (18)		CM92/41 270 (15)		PALB94/1C 846 (15)		RF93/75 368 (20)		RF93/77 797 (23)	
	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.
SiO_2	55.82	1.00	60.15	0.26	60.93	1.68	60.26	0.59	60.37	0.97	59.89	0.34	59.39	0.41
TiO_2	0.02	0.03	0.30	0.06	0.29	0.11	0.33	0.07	1.43	0.12	0.22	0.05	0.41	0.08
Al_2O_3	23.12	0.33	18.87	0.13	18.72	0.30	18.83	0.24	17.75	0.30	19.33	0.08	19.17	0.10
FeO	1.63	0.28	3.58	0.16	3.36	0.79	3.47	0.42	5.30	0.46	3.03	0.12	3.69	0.18
MnO	0.07	0.05	0.10	0.16	0.12	0.11	0.07	0.08	0.18	0.06	0.15	0.07	0.10	0.07
MgO	0.10	0.05	0.73	0.09	0.65	0.38	0.72	0.13	2.05	0.32	0.36	0.10	0.77	0.15
CaO	1.96	0.74	2.70	0.11	2.69	0.79	2.68	0.15	4.13	0.45	1.92	0.08	2.84	0.20
Na_2O	9.46	1.17	3.92	0.20	3.72	0.81	3.97	0.18	5.32	0.50	6.23	0.25	4.36	0.36
K_2O	7.26	1.01	9.11	0.16	9.04	0.56	9.14	0.18	3.18	0.32	8.10	0.10	8.75	0.30
Cl	0.56	0.05	0.53	0.04	0.48	0.15	0.53	0.06	0.28	0.04	0.77	0.04	0.50	0.07
K_2O/Na_2O	0.78	0.05	2.33	0.15	2.57	0.74	2.31	0.14	0.60	0.07	1.30	0.06	2.02	0.21
K_2O+Na_2O	16.72	0.74	13.03	0.15	12.76	0.63	13.11	0.17	8.50	0.61	14.33	0.23	13.11	0.25

4. DISCUSSION

4.1. Adriatic Sea

If we consider our results in comparison with those achieved with other analytical techniques (biostratigraphy, pollen analysis, isotopes, magnetostratigraphy, etc.) carried out in the PALICLAS project (Oldfield 1996, this volume), we observe that major changes in sediment composition occur in correspondence with the time boundaries that mark significant stages in the Adriatic Sea evolution. In fact the three zones that can be identified through chemostratigraphy (Figs 2-4) almost exactly correspond to Full Glacial, Late Glacial and Holocene times. Slight differences appear in PAL94/8 core, where biostratigraphic studies mark the late Glacial-Holocene transition at about 190 cm, and in core PAL 94/9, where erosion appears to be active in the lower portion of the core and the occurrence of coarse-grained sediments partially obscures the trends typical of the other finer-grained cores. Some elements, such as Cr, Co, Ni, Sr, and Cr/V, Sr/Ca ratios appear to be the most useful geochemical indices for the reconstruction of the palaeoenvironmental changes during the late Quaternary in the central Adriatic Sea (Calanchi *et al.* 1996a), whose evolution in terms of sediment supply can be summarised as follows.

Tab. 3. Results of provenance and age characterizations of tephra layers sampled in Albano and Nemi lakes and in central Adriatic Sea. Tephra layers are identified by depth in cm from the top of the core. For name and age of tephras see table 2 and: **SV** - "*Pompei* eruption" (1.9 kyr BP) or subplinian events between AV (3.7 kyr BP) and Pompei eruption from Somma-Vesuvius volcanic center. **20-11** and **C-14** - Unnamed events from the Campanian area in Paterne *et al.* (1988). Ages are uncalibrated years.

	Tephra	**SV**	**20-11**	**AV**	**AMS**	**C-1**	**C-2**	**Y-1**	**Y-5**	**C-14**	**C-20**
	Age kyr	1.9-3.7	3.4	3.7	4.4	9.8	12.3	14.2	35	41.8	67.5
Lake cores											
Albano	1E	---	---	354	---	---	---	717	---	---	---
	1C	---	---	352	---	---	---	846	---	---	---
	3A	---	---	525	---	---	---	---	---	---	---
Nemi	1B	---	---	450	---	---	---	---	---	---	---
Adriatic cores											
	PAL 8	---	---	---	124	---	208	353	---	---	---
	PAL 66	---	---	---	64	214	266	358	---	---	---
	PAL 77	---	---	---	140	---	530	---	---	---	---
	RF30	530	---	---	---	---	---	---	---	---	---
	RF75	---	---	---	---	---	---	---	368	---	---
	RF77	---	---	---	83	---	194	---	361	449	797
	CM41	---	60	---	70	---	240	420	---	---	
	CM42	---	---	---	---	---	190	---	450	---	710
	CM43	---	---	---	150	---	605	---	---	---	---

- In the Full Glacial period the Po River delta was near the core locations and MAD was a semienclosed basin with reduced water circulation (Trincardi *et al.* 1996, this volume): sediment composition was chiefly controlled by Po sediment supply, even if lateral input, from central Italian rivers, cannot be excluded. The contribution of this local supply is supported by the slight increase in siliciclastic elements in the upper half (350-250 cm) of the Full Glacial period in core PAL94/8, located on the western margin of the MAD close to the shore, an increase not recorded in core PAL94/66 that occupied a central position in the basin. As in the core PAL94/8 the chemical features of the sediment change above Etna Y-1 tephra layer (Calanchi *et al.* 1996b). We can state that the increase of local supply occurred about 14 kyr BP, probably as a consequence of a palaeoenvironmental change in the area. Data concerning this time interval are not available for core PAL 94/9, since our sampling plan did not include the lowermost part of the core, the older one (about 15 kyr BP from ^{14}C datings, Trincardi *et al.* 1996, this volume).

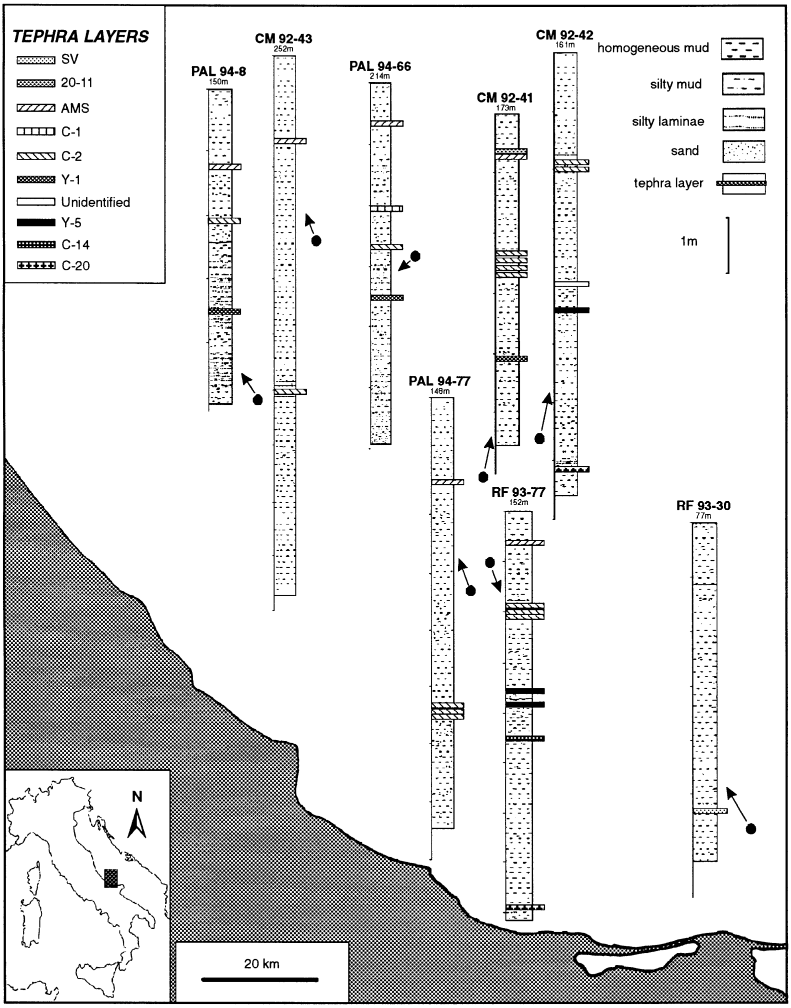

Fig. 6. Core logs indicating the stratigraphic distribution of tephra layers in central Adriatic Sea (Trincardi *et al.* 1996, this volume). For provenance and age of tephras see legend in tables 2-3.

- The transition to Late Glacial is associated with the marine transgression, so changes in water depth and water circulation patterns are expected to have occurred: this is marked by a slight but clear transition towards the values observed for the present day sediments, characterised by slightly higher carbonate and lower dolomite contents in the deeper cores, and by higher Cr, Co and Ni concentrations. The increase in Cr, Co and Ni background values is possibly related to the input of mafic and ultramafic sediments, derived from the ophiolitic outcrops of the Dalmatian region and carried to the MAD by the anticlockwise water circulation patterns active in the Adriatic Sea. Such a provenance hypothesis is further supported by the observation that the metal concentrations decrease towards the Italian coastlines (PAL94/66 >PAL94/8 >PAL94/9).

- The transition to Holocene, that in PAL94/66 occurs close to a tephra layer identified as C-1 (9.8 kyr BP), does not seem to strongly affect sediment chemistry, being similar to the previous period. A strong increase of carbonate supply (but not of dolomite) is typical of this section, and the low dolomite content agrees with the minor importance of the northern sediment supply compared to eastern and western ones. Holocene sediments in core PAL94/9 record instead an higher silicate fraction, possibly deriving directly from the Apenninic rivers, but display the same trend of other cores in the dolomite-calcite ratio.

4.2. Lake Albano

Based on chemical depth profiles of PALB94/1E core, some broad zones with peculiar geochemistry can be identified (Fig. 5), and the environmental evolution of Lake Albano area can be inferred as follow.

- Zone 1 - base to about 1100 cm - This zone is characterised by the highest values of Ca and CO_2 in the core. The carbonate content is not homogeneous, as layers rich of carbonates alternate irregularly with others where siliciclastic phases and amorphous silica are prevalent. The silicate elements (A group) decrease upwards moving from the bottom sediment formed by volcanic rock fragments.
- Zone 2 - 1100 cm to 695 cm - Sharp increase of the A group elements contents in the lower samples, followed by stabilisation of their values; irregular increase of the B elements (carried mainly by the organic matter), except for Br, and strong decrease of carbonate elements. The chemical variations observed point to a change in the sediment composition, with higher terrigenous supply from the catchment area probably as a result of increased erosion; the increase of the B elements, but not of Br, mainly enriched in plants (Kabata-Pendias & Pendias 1992; Robinson *et al*. 1993), testifies to the development of lacustrine organism. All this supports the onset of a climatic change towards better conditions (end of Full Glacial); the disappearance of carbonates, coupled with increase of S content, may indicate some chemical variation inside the lake (lower pH values of water) due to changes in the fluid vents from deep (volcanic gases?).
- Zone 3 - 695 cm to 520 cm - The elements of the A group decrease gradually while those of the B group, except for Si, increase. This may testify to a decline in surface erosion, a consequence of the stabilisation of crater slopes, due to the terrestrial vegetation development (supported by the sharp enrichment of Br), and growth of within-lake biological productivity. Stabilisation of Si values, coupled with increase of Si/Al ratios, may result from the balance between lower terrigenous supply and higher productivity of siliceous organisms. The above

observations point out the increase of the environmental effects of a warmer and more humid climate (from Late Glacial to Holocene).

- Zone 4 - 520 cm to 405 cm - This interval is characterised by the lowest values of silicate related elements and by the highest values of the B group elements and of biogenic silica (Tab. 1), testifying to minimum catchment erosion and maximum biological productivity, both in and around the lake (*cf* Ryves *et al*. 1996, this volume; Guilizzoni *et al*. 1996). The opposite behaviour of Th and U suggests that these elements are associated with different carriers, and support, according to with some palaeoredox indices (V/Cr ratio; Aut. U, Tab. 1), the development of anoxic conditions in the lake environment favourable to the precipitation of U compounds and to the preservation of organic matter (water stratification?).
- Zone 5 - 405 cm to 62 cm - The main features of the bottom of this zone are the sharp breakdown of parameters linked to biological productivity and the increase of those typical of terrigenous supply. As Br values and Br/biogenic-silica ratios do not change or slightly increase, the productivity breakdown does not affect the terrestrial vegetation, but only within-lake organisms. The abrupt change of sediment geochemistry has not a simple meaning. It may reflect the development of conditions not favourable to life, such as variations in fluid discharges from depth or sudden and strong increase catchment erosion (forest clearance and fire by human impact ?). It may also reflect the sediment erosion event (hiatus) which seems to characterise this zone *ca* 4100 yr BP to *ca* 7500 yr BP (Chondrogianni *et al*. 1996, this volume). The chemistry of the upper sediment suggests a stabilisation of the balance between erosion and productivity, with a new impulse of productivity at about 134 cm, as the coherent increase of the B group elements points out.

5. CONCLUDING REMARKS

The palaeoenvironmental changes occurred during late Quaternary in central Italy are really recorded in both Adriatic and lake sediments by their geochemical features, but with some differences. During the transition from Full Glacial to Holocene times, the warmer climate and ice melting acted mainly on the biological productivity and sea-level rise, with consequences on the erosion rate of the catchment areas and on the location of the coast line. Also the increase in human impact (e.g., forest clearance and fires) played an important role, at least for lake catchment erosion. In this research the main geochemical effects recorded by lake sediments are related to changes in organic/inorganic matter ratios, due to differences in productivity and terrigenous supply. Those found in the marine sediments reflect the values of some mineral and trace element, testifying to the evolution of river inputs and of marine hydrodynamics.

Useful indices of Lake Albano evolution appeared to be (Tab. 1 and Fig. 5): total organic content (LOI* <650°C), biogenic silica and Br for biological matter; Al, Y and Zr/Rb ratio for terrigenous clastic material; LOI*/Al for organic/terrigenous material ratio; autigenic U and V/Cr for redox conditions. As regards the Adriatic sediments the more promising geochemical indices of palaeoenvironmental changes in the late Quaternary appeared Cr, Co, Ni, Sr, and Cr/V, Sr/Ca ratios (Calanchi *et al*. 1996a).

The occurrence of tephra layers interbedded in both lakes and sea samples allowed the determination of some chronostratigraphic markers for between lake, marine-lake and between Adriatic core correlations. Among them Y-1 layer (14.2 kyr uncalib. BP) from Etna volcano results the most widespread both in lake and sea cores. The age attribution, based on comparison of the studied tephra with those of literature, supplied also an indirect method of dating the sediments in the 2-70 kyr BP age range.

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