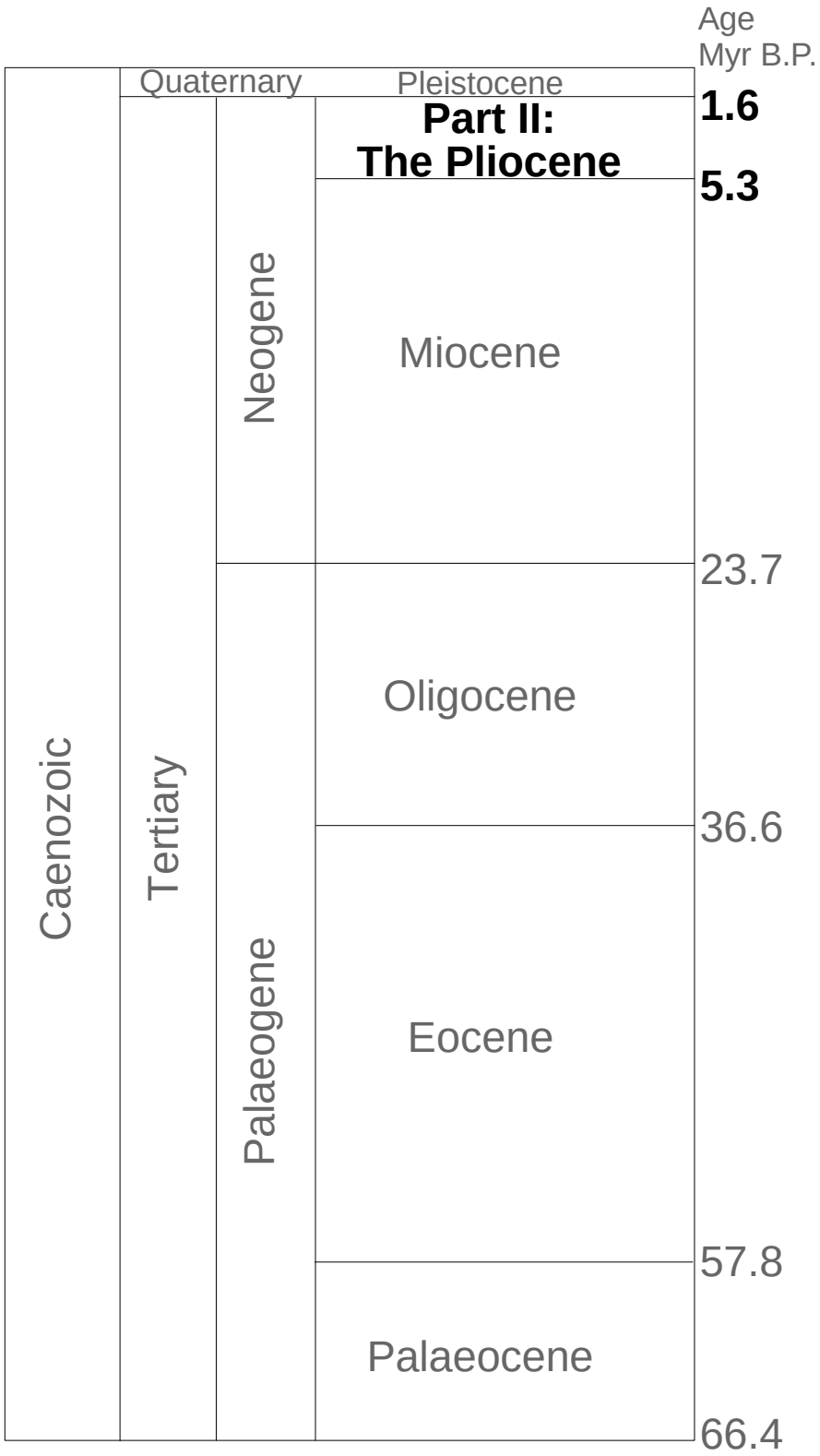

"The Mediterranean is beautiful
in a different way from the ocean,
but it is as beautiful."

Victor Hugo

Chapter 4

Diatomites at Lido Rossello: Geochemistry and implications for formation models of the "Trubi" marls

I.A. Nijenhuis, L.J. Lourens, G.J. de Lange

Abstract - The geochemistry and micropalaeontology of three coeval marine sedimentary cycles of the Pliocene "Trubi" formation have been investigated in two land sections. The Punta di Maiata and the nearby Lido Rossello sections at Sicily show the same grey-white-beige-white coloured quadripartite carbonate cycles. At Lido Rossello, however, a laminite and a diatomite are intercalated in this pattern.

Palaeoproductivity, as inferred from barium contents, was high during deposition of the grey layers, the diatomite and the laminite. In contrast, the planktonic foraminiferal shell flux is low in the grey layers. Dilution by clays, which has occurred by aeolian input in the beige layers, and by fluviatile input in the grey layers, is insufficient to explain the low shell flux in the grey layers, but may account for the decrease in total carbonate content in the beige layers. Carbonate dissolution has taken place in the grey layers and the laminites, as evidenced by strontium mobilization peaks around these layers.

Apart from increased productivity, the presence of a local depression at Lido Rossello may have contributed to the formation of the laminite and the diatomite.

This chapter will be submitted together with *Lourens et al. [in prep.]* to *Paleoceanography*.

Introduction

Rhythmic limestone-marl cycles are common in the geological record *[e.g. Einsele and Seilacher, 1982, and references therein]*, and are often driven by variations in the Earth's orbit *[e.g. Fischer, 1980; De Boer, 1991]*. These so-called periodites may develop when sediments are deposited under oxic conditions with a carbonate / clay ratio in the order of four, and when the alternating beds are too thick to become obliterated by bioturbation *[Einsele, 1982]*. The origin of periodites is discussed in terms of carbonate productivity and dissolution, terrestrial dilution, and diagenetic processes such as pressure solution *[e.g. Einsele, 1982]*.

The marls of the "Trubi" formation of the Sicilian and Calabrian Pliocene are a special example of such periodites. These sedimentary rocks vary not only in carbonate, but also in organic carbon (C_{org}) content. As a result, quadripartite cycles occur, consecutively consisting of a grey marl, slightly enriched in C_{org}, a white limestone, a beige marl (poor in C_{org}), and another white limestone. More commonly, Mediterranean Neogene and Quaternary sediments are characterized by bipartite cycles consisting of limestones or marls alternating with sapropels, sedimentary layers containing more than 2% C_{org}. Both quadripartite and bipartite cycles have been linked to the precession of the Earth's equinoxes, the grey layers and sapropels representing humid periods at times of precession minima (Northern Hemisphere insolation maxima) *[Hilgen, 1991a, b; Lourens et al., 1996a]*. Mediterranean sapropels have been studied intensively in the last few decades *[e.g. Kidd et al., 1978; Cita and Grignani, 1982; Rossignol-Strick et al., 1982; Calvert, 1983; De Lange and Ten Haven, 1983; Mangini and Schlosser, 1986; Rohling and Hilgen, 1991; Nijenhuis et al., 1996 (Chapter 2)]*. Their origin is thought to be the result of increased continental runoff, which on the one hand supplies nutrients, raising productivity, and on the other hand stabilizes the water column, possibly resulting in anoxic bottom waters and improved organic matter preservation. Quadripartite cycles have received much less attention. *De Visser et al. [1989]* conducted an integrated low-resolution micropalaeontological, palynological, geochemical and clay mineralogical research on four cycles of the Punta di Maiata section. They concluded that an alternation of increased terrestrial input (grey layers) and decreased carbonate production (beige layers) caused the carbonate cycles. Based on a combined geochemical and micropalaeontological survey of the first sapropel-containing carbonate cycle of the Narbone formation which directly overlies the "Trubi" marls, *Van Os et al. [1994]* concluded that productivity changes were the main cause of the cyclicity: low productivity in the beige layers, intermediate (mainly carbonate) productivity in the white layers and very high (mainly organic / opal) productivity in the grey layers. *Thunell et al. [1991]*, on the other hand, concluded on the basis of mainly foraminiferal data that marl-limestone duplets in the Calabrian "Trubi" formation were caused by low productivity in the marls (equivalent to the grey layers) and upwelling-type conditions in the limestones (equivalent to the beige and white layers).

Whatever the best model may be, it seems that the origin of the "Trubi" quadripartite cycles lies in an intricate interplay of the processes of marine productivity, terrestrial dilution,

and carbonate dissolution. Further constraining these processes is essential to our understanding of the formation of these sediments and their link to climatic variations. An excellent opportunity for achieving this may lie in the occurrence of local deviations in the monotonous grey-white-beige-white successions. The irregular occurrence of six laminated intervals (some containing diatoms) in cycles 26-31 of the Lido Rossello section *[Brolsma, 1978]* is such a local deviation. These laminites are absent in coeval sediments of the nearby Punta di Maiata section. We conducted an integrated high-resolution geochemical and micropalaeontological survey of three sedimentary cycles at Lido Rossello (containing the top two laminites) and their lateral equivalents at Punta di Maiata (where these laminites are absent). It was found that the laminites are productivity events unrelated to precessional forcing *[Lourens et al., in prep.]*. In this paper, we will further constrain the processes involved in the formation of the laminites, and discuss the implications of their occurrence for existing formation models of the "Trubi" marls.

Material and methods

Geological setting

The Lido Rossello and Punta di Maiata sections are exposed along the beach at the south coast of Sicily in some four kilometres of continuous cliff outcrops (Fig. 4.1A). These outcrops cover the lower part of the Pliocene "Trubi" formation, and the contact with the underlying upper Miocene "Arenazzolo" formation is locally visible. The cliff-face is dissected by numerous NW-SE trending faults (every fifty metres), which show displacements of up to fifteen metres *[Brolsma, 1978]*.

The marine sediments of the "Trubi" formation have been deposited at a water depth between 500 and 800 metres *[Brolsma, 1978]*. Weathered sediments are characterized by a distinct grey-white-beige-white colour alternation, with the grey and beige layers being less indurated. The fresh sediments show a markedly different colour alternation of dark blue - light blue (or white) - light blue with dark blue bands - light blue.

At Lido Rossello, approximately twenty-nine metres above the local base of the "Trubi" formation, six brownish-rose, finely bedded limestone marls are intercalated *[Brolsma, 1978]*. These laminated beds vary in thickness from 10 to 145 cm and contain, with the exception of the uppermost bed, siliceous organisms (radiolaria and diatoms) *[Zachariasse et al., 1978]*.

Sampling

Samples were taken during three campaigns. In October 1994, we sampled an interval at Lido Rossello wich contains carbonate cycles 29 and 30 (cycle coding after *Langereis and Hilgen, [1989]*) and the uppermost laminated bed (no. 6 of *Brolsma [1978]*), which has a distinct brown colour. In June 1995 we sampled the time-equivalent cycles at Punta di Maiata (about one kilometre to the southeast) and extended our 1994 sampling trajectory at Lido Rossello downwards. This latter interval was sampled in another gully approximately ten metres to the

east with respect to the 1994 trajectory, and contains carbonate cycle 29, part of cycle 28, and a second laminated interval (no. 5 of *Brolsma [1978]*). In August 1996, we sampled the time-

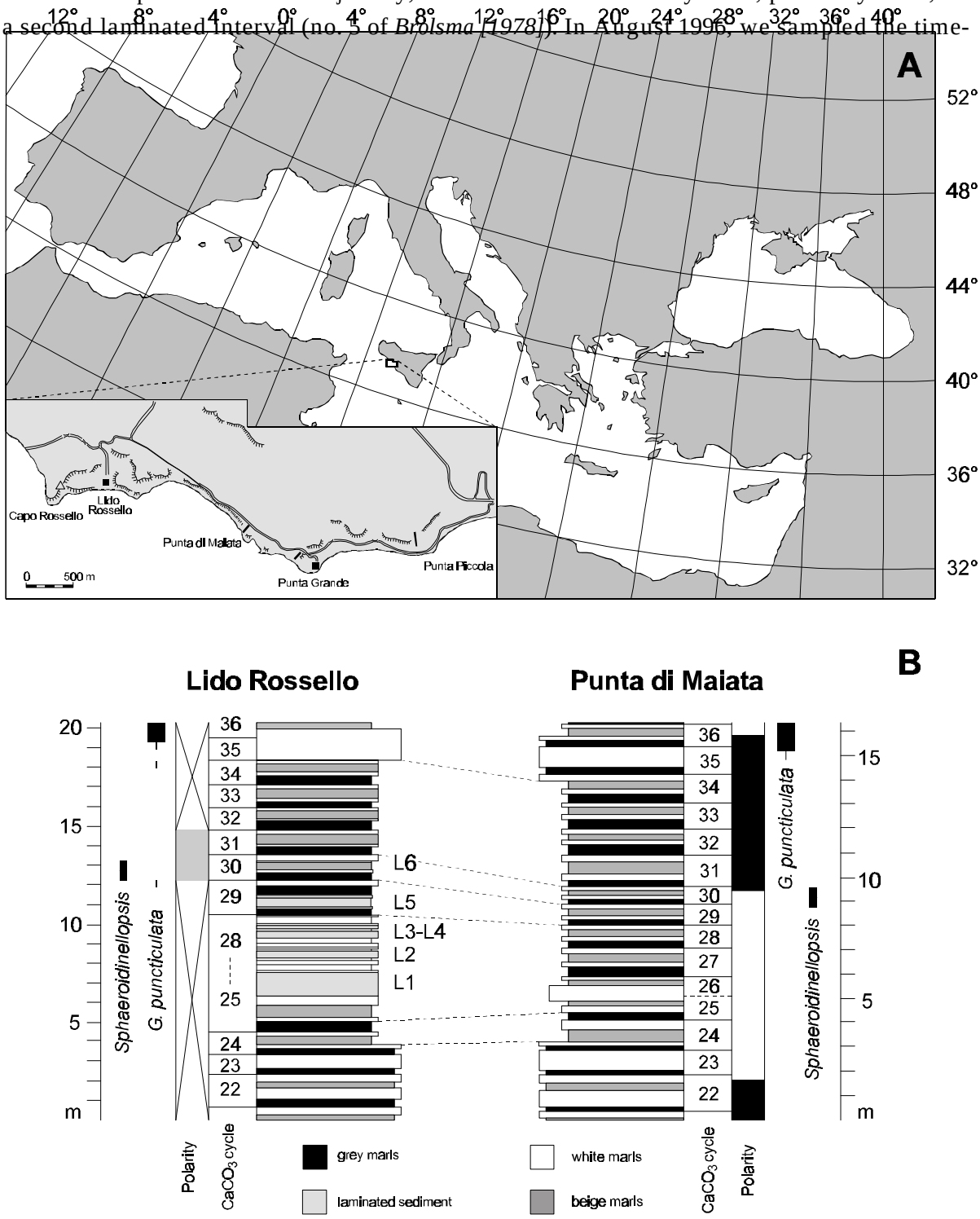

Figure 4.1 *Location of the sections (A) and composite stratigraphic columns of carbonate cycles 22-36 at Lido Rossello and Punta di Maiata (B). The laminated intervals at Lido Rossello as described by Brolsma [1978] are indicated by L1-L6.*

equivalent interval at Punta di Maiata in an outcrop approximately fifteen metres to the east of the 1995 sampling trajectory. A composite stratigraphic column of cycles 22-36 in both sections is shown in Fig. 4.1B.

Considerable effort was taken to remove the weathered surface to expose the fresh sediment. After that, small cores with a diameter of 2.5 cm were drilled and packed in aluminium foil. During the 1994 campaign, separate samples for geochemical purposes were taken by scraping off sediments parallel to the bedding plane using a stainless steel spatula. These samples were transported in glass jars. All other geochemical analyses were performed on the drilled cores after cleaning their surface by scraping with a stainless steel knife.

Micropalaeontology

Counts of planktonic foraminiferal species, siliceous organisms and palynomorfs were made on splits from the 125 to 595 µm fraction. Between 200 and 400 specimens of planktonic foraminifera were picked per sample, mounted on Chapman slides, identified and counted. For each slide, we also counted the amount of siliceous organisms, benthic foraminiferal specimens and palynomorfs. Counted species / groups are: *Globigerinoides obliquus*, *Globigerinoides trilobus*, *Globoturborotalita apertura* + *Globoturborotalita nepenthes*, sinistral- and dextral-coiled *Neogloboquadrina acostaensis*, *Sphaerodinellopsis seminulina* + *Sphaerodinellopsis subdehiscens*, *Globigerina falconensis*, *Globigerina quinqueloba*, *Globigerinata glutinata*, *Orbulina universa*, *Globigerinella siphonifera* and *Globorotalia margaritae*.

In the laminated intervals, organic compounds of small spherical objects were observed, and larger ones which were always wrinkled. *Brolsma [1978]* had these forms tentatively identified by G.T. Boalch as possible representatives of the genus *Pachysphaera* (division Chlorophyta (green algae), class Prasinophyceae).

Geochemistry

The samples were freeze-dried and powdered in an agate mortar. After removing inorganic carbon with 1 M HCl, C_{org} was measured with a Fisons NA 1500 NCS analyser. Stable organic carbon isotopes ($\delta^{13}C_{org}$) were determined with a Stable Isotope Ratio Analyser (VG SIRA 24), and are reported relative to the PeeDee Belemnite (PDB) standard. The carbonate content was determined gas-volumetrically. Opal analyses were performed on selected samples, following the method of *Müller and Schneider [1993]*, using a Technicon TRAACS 800 auto-analyser. For major, minor and trace element analyses, a 250 mg sample was digested in 10 ml of a 6.5 : 2.5 : 1 (v / v) mixture of $HClO_4$(60%), HNO_3(65%) and H_2O, and 10 ml HF (40%) at 90°C. After evaporation to dryness on a sand bath at 190°C, the residue was dissolved in 50 ml 1 M HCl. The resulting solutions were analysed with a Perkin Elmer Optima 3000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) for Al, Ca, Fe, S, Ti, Ba, Sr, Ni, and V. For selected samples from Lido Rossello, these solutions were also analysed for As and Se with a Perkin Elmer 3100 hydride-Atomic Absorption Spectrometer (AAS).

All results were checked with international and house standards. Absolute standard deviations in $\delta^{13}C_{org}$ analyses are below 0.2‰. Relative standard deviations in duplicate measurements are lower than 1% for carbonate analyses, and lower than 5% for C_{org} and ICP duplicate measurements. As and Se were measured in triplicate with a standard deviation below 10%.

Age model

We assigned astronomical ages to the midpoints of the grey layers of Punta di Maiata as given by *Lourens et al. [1996a]*. Hereafter, we tuned the Lido Rossello succession to Punta di Maiata by using the characteristic faunal patterns of three planktonic foraminiferal species / groups: *Sphaeroidinellopsis seminulina* + *Sphaeroidinellopsis subdehiscens*, *Globigerinoides trilobus* and *Globorotalia margaritae*. A comparison between the sedimentation rates of the two localities is shown by their ratios (Fig. 4.2). This ratio indicates that the sedimentation rates of both sections are almost similar during deposition of cycles 30, 31 and the top of cycle 28, whereas they are significantly higher at Lido Rossello during deposition of cycle 29.

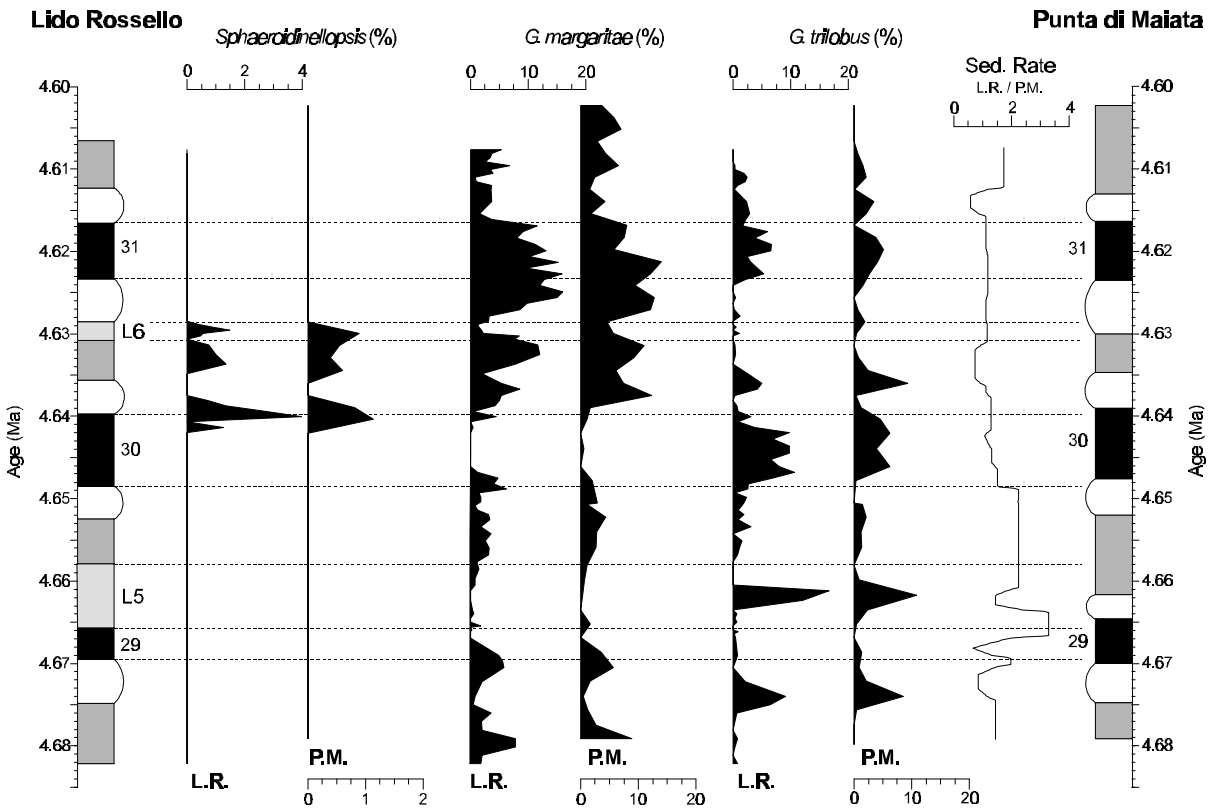

Figure 4.2 *Abundance of the planktonic foraminifera species used for constructing the age model, and the ratio of the inferred sedimentation rates at Lido Rossello and Punta di Maiata.*

Results

Micropalaeontology

Distribution of the planktonic foraminiferal species used in constructing the age model are shown in Fig. 4.2; the total foraminiferal shell flux per cubic centimetre is shown in Fig. 4.3. Distribution patterns of other individual planktonic foraminiferal species are reported elsewhere *[Lourens et al., in prep.]*. The ratio of benthic to total foraminifera is highest in the grey layers and low in the laminites. Diatoms and radiolaria have only been found in the lower part of the diatomite in cycle 29 at Lido Rossello.

Geochemistry

First, the geochemistry of the "normal" grey-white-beige-white sediments at Punta di Maiata will be reported. Subsequently, we will show in how far this pattern is different at Lido Rossello, due to the occurrence of the diatomaceous laminite in the white intervals of cycle 29 ("the diatomite") and the brown laminite in the beige interval of cycle 30 ("the laminite").

Punta di Maiata - Contents of C_{org} (Fig. 4.4) are low in the white and beige layers (~0.08%) and high in the grey layers (up to 0.30%). Barium (shown as $Ba^{*}=(Ba_{sample} / Al_{sample})\times Al_{average}$ (Fig. 4.4) in order to correct for carbonate dilution effects) covaries with C_{org}, but the transitions to high values are more abrupt. The carbonate content of the sediments is high, on average 77% (representative for the grey layers), varying between ~83% in white and ~70% in the beige layers (Fig. 4.3). Note that the shell flux and the carbonate content do not show the same pattern. The $Sr / CaCO_3$ ratio (Fig. 4.3) is constant, but slightly higher in the top and bottom of the grey layers than in the middle of these layers. Aluminium (Fig. 4.5) correlates inversely with $CaCO_3$. The Ti / Al curve is of a duplet type, with low values in grey and high values in beige layers, the inverse of the 65°N summer insolation pattern (Fig. 4.5). Sedimentary Fe^{*} and S contents are nearly constant (Fig. 4.6). There is considerable scatter in the trace element data, but the contents of Ni and V (shown as ratios to Al; Fig. 4.7A) are higher in the grey layers than in the white and beige sediments.

Lido Rossello - The grey-white-beige-white cyclicity patterns at Lido Rossello are almost identical to those observed at Punta di Maiata, but the carbonate contents are slightly lower (Fig. 4.3). At Lido Rossello, $Sr / CaCO_3$ ratios are higher, and peaks around the grey interval of cycle 30 are much more pronounced than they are at Punta di Maiata (Fig. 4.3). Except for the part above the brown layer, Fe^{*} and especially S are higher at Lido Rossello (Fig. 4.6). In this section $\delta^{13}C_{org}$ and opal have been analysed as well. These parameters do not show a correlation with the grey-white-beige-white lithologies (Fig. 4.4). The samples at 4.634 and 4.678 Ma show particularly negative $\delta^{13}C_{org}$ values. The presence of a constant amount of 1 wt% opal in these sediments is not accompanied by the presence of siliceous organisms, and may, therefore, be an artefact of the indirect method used for its analysis *[Müller and Schneider, 1993]*.

The diatomite in cycle 29 stands out in the Lido Rossello profiles because it is characterized by the highest contents of C_{org} (up to 0.8%), opal (4%), Ba (900 ppm), Fe, S, V, As and Se (Figs. 4.4, 6 and 7). The lower, well-laminated part of the diatomite is clearly enriched

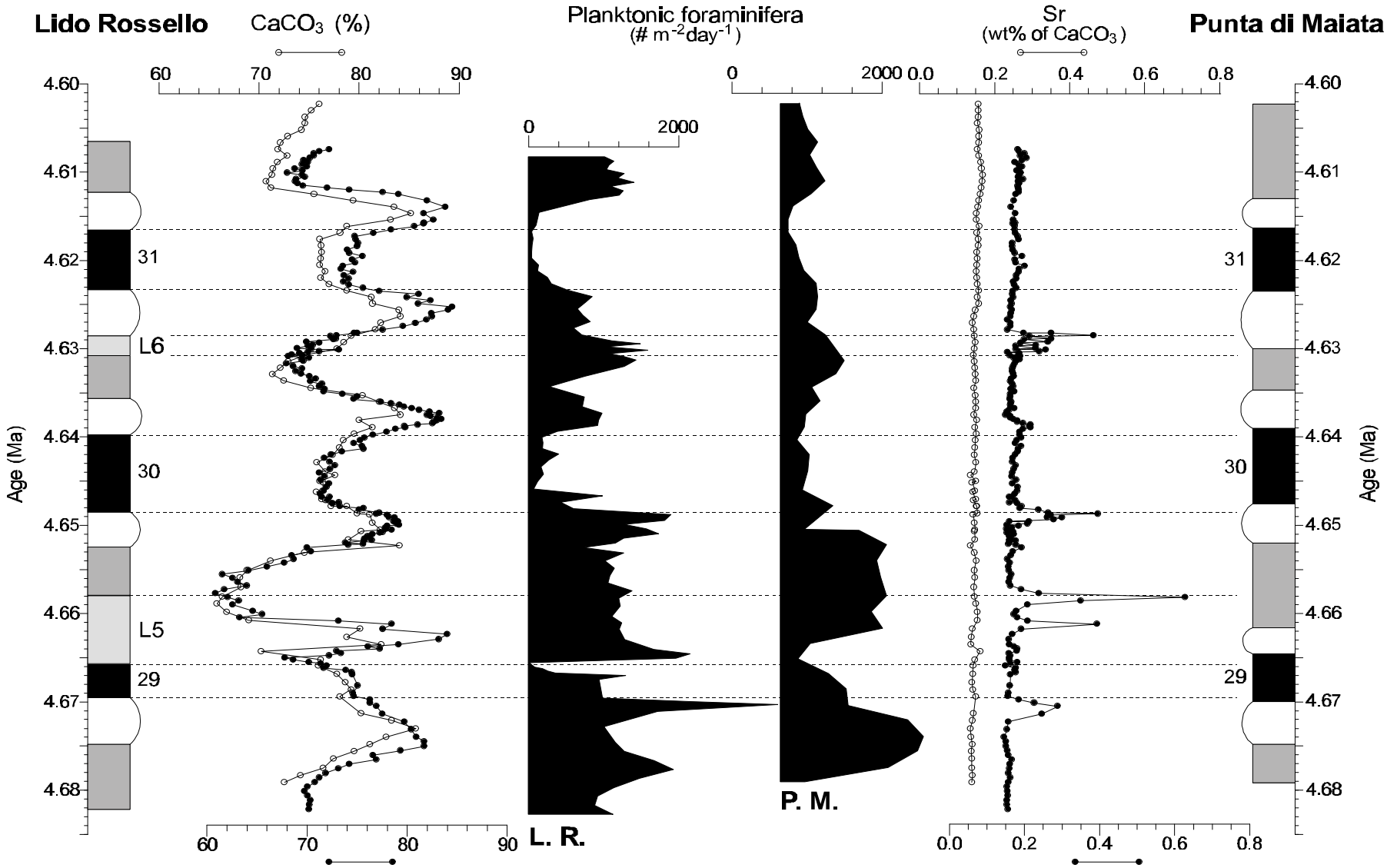

Figure 4.3 *Profiles of $CaCO_3$, flux of planktonic foraminifera, and $Sr/CaCO_3$ at Lido Rossello (closed symbols/L.R.) and Punta di Maiata (open symbols/P.M.). Note that there is a small offset in the horizontal axes of the $CaCO_3$ and $Sr/CaCO_3$ profiles.*

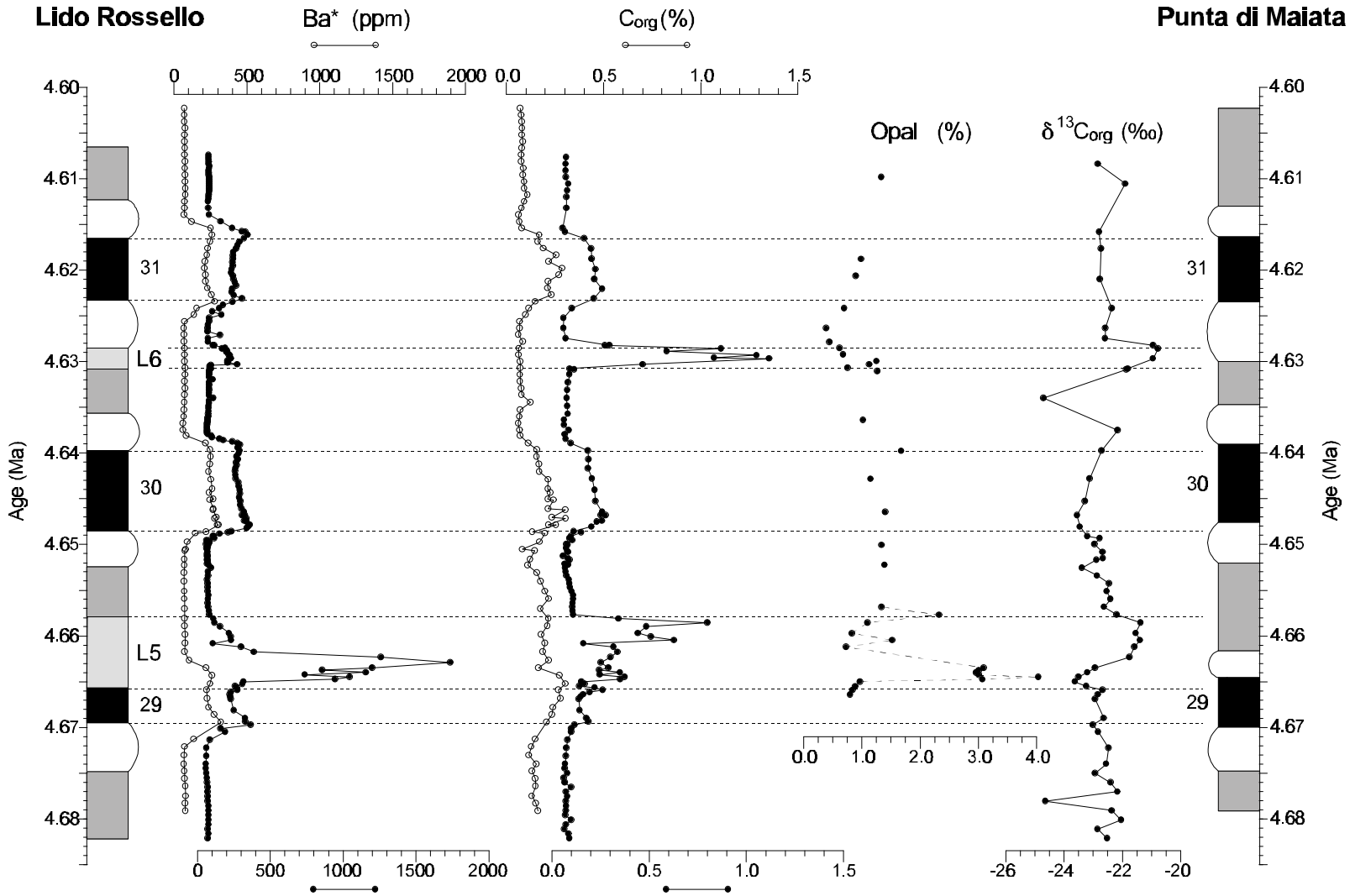

Figure 4.4 *Profiles of Ba* and C_{org} at Lido Rossello (closed symbols) and Punta di Maiata (open symbols), and opal and $\delta^{13}C_{org}$ at Lido Rossello only. Note the small offset in the horizontal axes of the Ba and C_{org} profiles.*

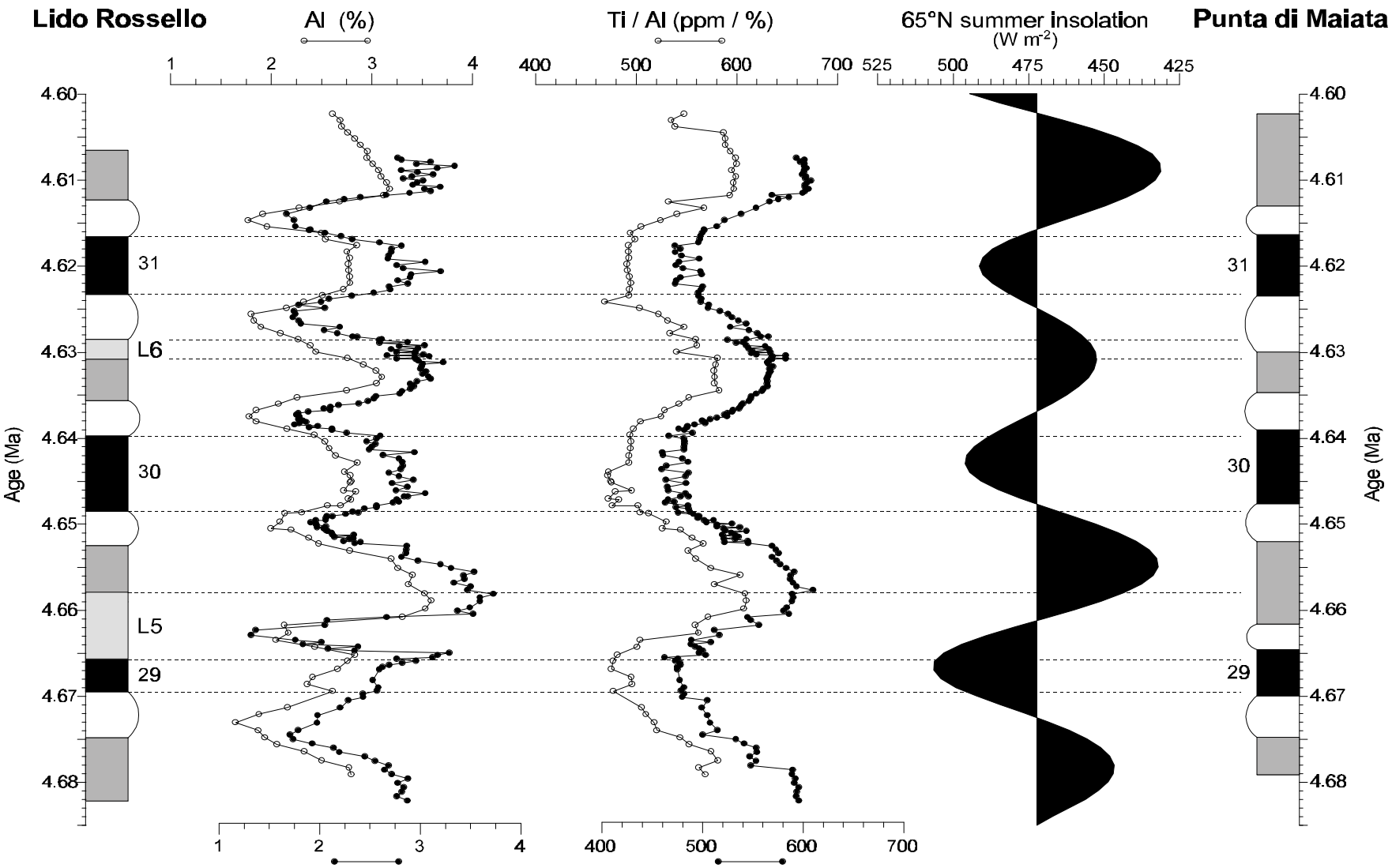

Figure 4.5 *Profiles of Al and Ti/Al at Lido Rossello (closed symbols) and Punta di Maiata (open symbols) and 65° N summer insolation. Note that there is a small offset in the horizontal axes of the Al and Ti/Al profiles, and that the horizontal axis of the insolation curve is reversed.*

in opal, and is further characterized by highest Ba, trace element, Fe and S contents, but by intermediate C_{org} contents. In the upper part of the diatomite, lamination is less well developed, and highest C_{org} contents are reached. Additionally, the transition from the lower to the upper part is characterized by a shift from more to less negative $\delta^{13}C_{org}$ values (Fig. 4.4). The highest $Sr/CaCO_3$ peaks are observed around the upper part of the diatomite. The brown laminite has C_{org} contents comparable to the diatomite, and Ba enrichments comparable to those in the grey layers. Opal and trace elements are not enriched in this layer.

Discussion

The observed differences in geochemical parameters in cycles 28-31 between Lido Rossello and Punta di Maiata appear to be related to the occurrence of the laminite and the diatomite in between the typical "Trubi" grey-white-beige-white sediment alternations. Here, the occurrence of the laminated intervals will be discussed in terms of the different models invoked to explain the carbonate cyclicity. In particular, we will focus on the relative importance of productivity, dilution, and carbonate dissolution processes.

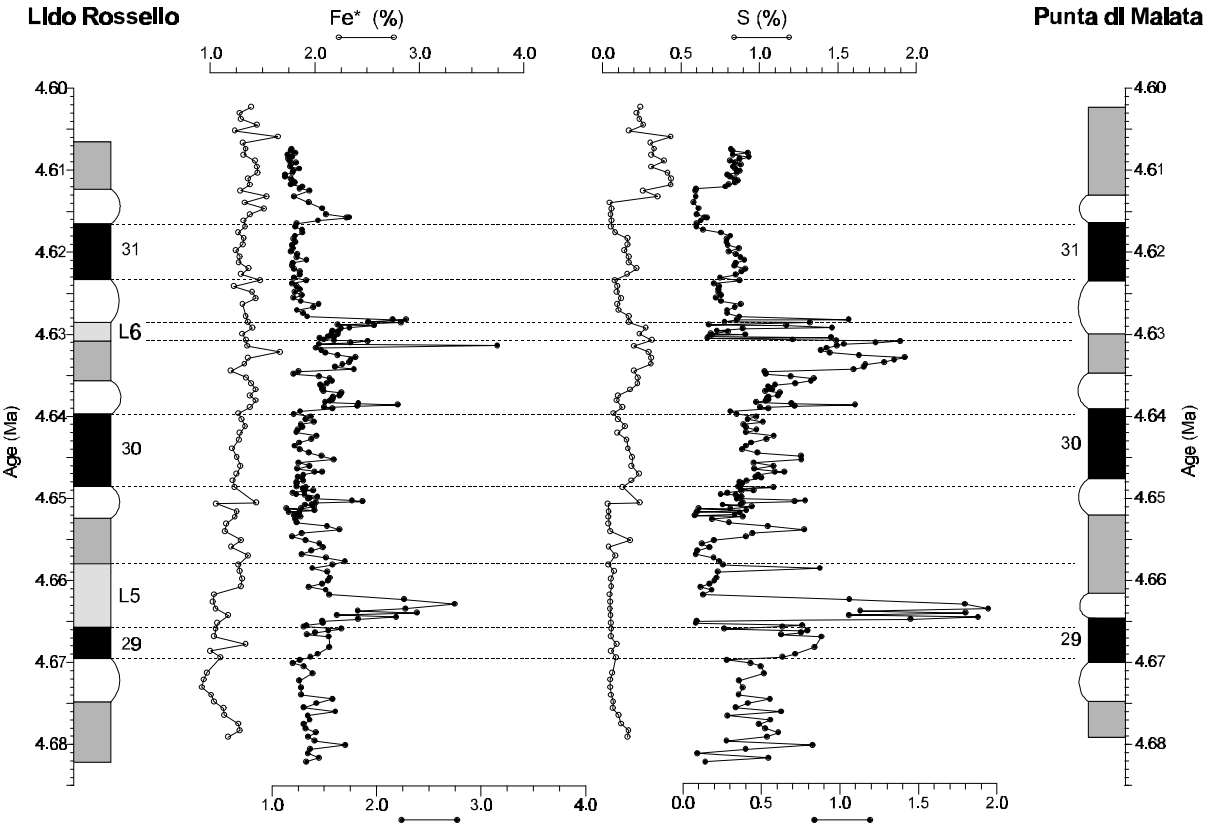

Figure 4.6 *Profiles of Fe* and S at Lido Rossello (closed symbols) and Punta di Maiata (open symbols). Note the small offset in the horizontal axes.*

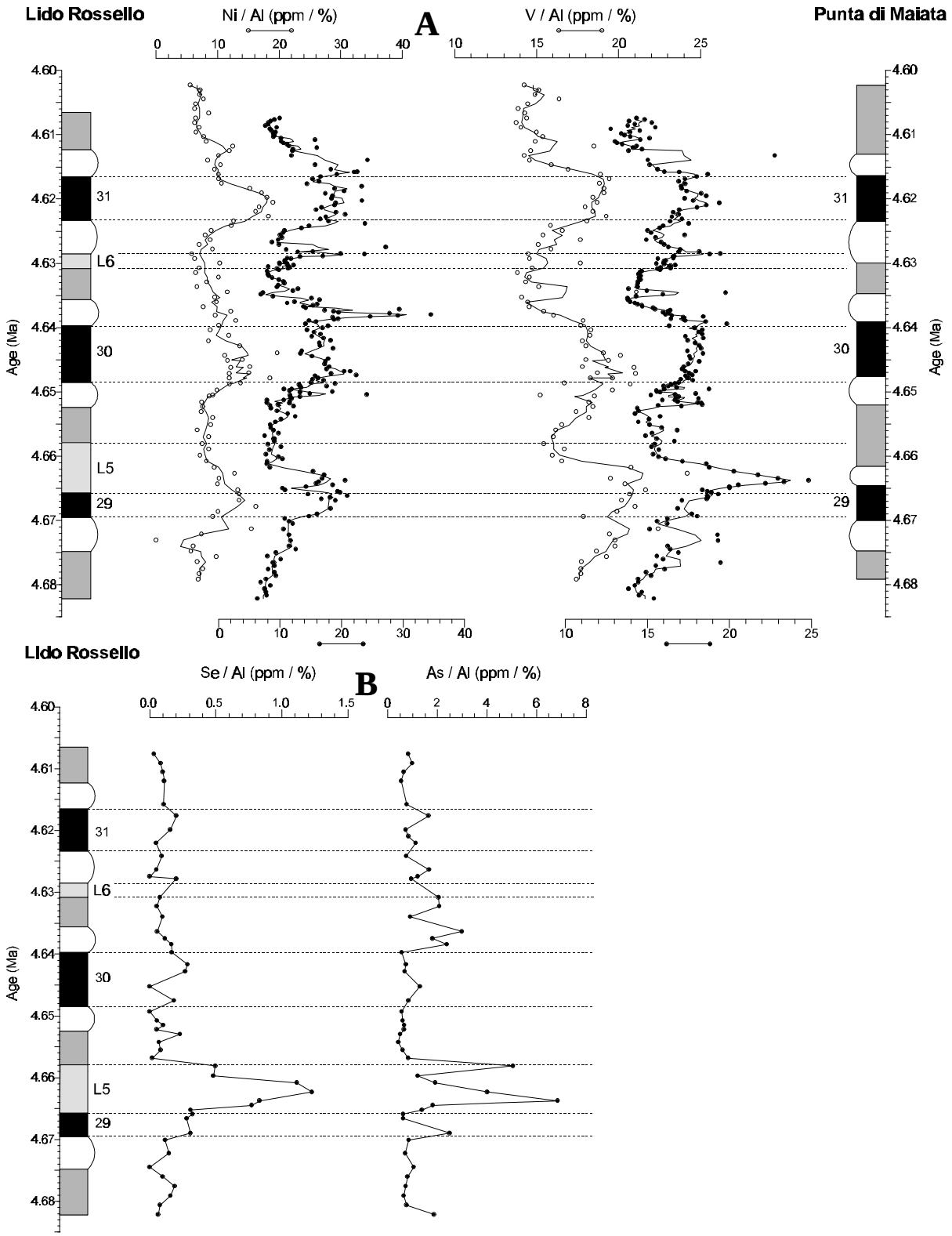

Figure 4.7 *A: Profiles of Ni/Al and V/Al at Lido Rossello (closed symbols) and Punta di Maiata (open symbols). Solid lines are 3-point moving average curves. Note the offset in the horizontal axes.*
B: Profiles of Se/Al and As/Al at Lido Rossello.

Productivity

Sedimentary barium is considered a reliable palaeoproductivity indicator. It originates from barite formed in settling particles with microenvironments containing decaying organic matter *[Dehairs et al., 1980; Dymond et al., 1992]*. In the "Trubi" marls, Ba^* covaries well with C_{org}, both being higher in the grey layers, and low and constant in the beige and white layers. The existence of a constant relation between Ba^* and C_{org} is indicated by almost identical levels of these parameters in Lido Rossello and Punta di Maiata. The elevated Ba^* values in the grey layers and the laminated intervals at Lido Rossello, therefore, indicate that these layers were formed under conditions of increased productivity. This is confirmed by the oxygen and carbon stable isotope composition of different planktonic foraminiferal species, which indicate higher nutrient levels during deposition of these layers *[Lourens et al., in prep.]*. Moreover, the high Ba contents within the diatomite at Lido Rossello are accompanied by enhanced opal contents and the occurrence of diatoms and radiolarians. These siliceous organisms are abundant in highly productive surface waters associated with, e.g., upwelling *[Takahashi, 1986]*.

High Ba contents are accompanied by high planktonic foraminiferal shell fluxes in the laminated intervals at Lido Rossello, but by low shell fluxes in the grey layers (Fig. 4.3). Moreover, the shell flux is higher at Lido Rossello than at Punta di Maiata, whereas the Ba contents are almost identical. In other words, high surface water palaeoproductivity inferred from Ba contents and from planktonic shell fluxes are not always related. Similar low carbonate shell fluxes associated with high Ba contents in a grey layer of a younger carbonate cycle in the nearby Punta Piccola section (Fig. 4.1A) have been attributed to outcompetition of calcareous organisms by siliceous plankton and opportunistic foraminifera under high productivity conditions *[Van Os et al., 1994]*. The absence of the expected diatoms and radiolarians in those grey layers has been explained by dissolution of opal *[Van Os et al., 1994]*. The presence of a diatomite at Lido Rossello shows that siliceous organisms can be preserved in this setting. The absence of diatoms and radiolarians in the grey layers of Lido Rossello, therefore, suggests that they were never abundantly present in these layers. Furthermore, the presence of siliceous organisms apparently does not necessarily result in low carbonate shell fluxes. Therefore, the low shell flux in the grey layers is more likely to be explained by dilution with clays or dissolution of carbonates. We will now discuss these processes.

Dilution

Total sedimentation rate probably did not fluctuate much in the Lido Rossello and Punta di Maiata sections (Fig. 4.2). Nevertheless, variations in the relative contributions of the marine (carbonate) and terrestrial (clay) fractions may have occurred, leading to dilution effects.

A striking observation is the sinusoidal bipartite cyclicity of the Ti/Al curve (Fig. 4.5) in these quadripartite sedimentary cycles. This ratio is highest in the beige layers, and lowest in the grey intervals, and is, therefore, the opposite of the insolation curve (Fig. 4.5). Titanium is representative of heavy minerals, which are thought to be mainly transported to deep marine sediments by wind *[e.g. Boyle, 1983; Shimmield, 1992]*. Therefore, lower Ti/Al values indicate

a relatively higher contribution of river with respect to wind input. This explains the inverse correlation between the Ti / Al profile and the insolation curve: at precession minima (insolation maxima, grey layers) climate around the Mediterranean is relatively wet, resulting in high river and low wind input, whereas the reverse situation occurs at precession maxima (insolation minima, beige layers).

The relative changes in aeolian and fluviatile input can be quantified using the Ti / Al curve once the Ti / Al value of wind-blown dust and of river particles is known. The Ti / Al value of recent dust storms in the Mediterranean area is 623 ±75 (ppm / %; *Bonelli et al. [1996]; Güllü et al. [1996]*). The Ti / Al value of suspended matter in world rivers varies between 485 and 667 *[Gordeyev and Lisitsyn, 1978; Martin and Meybeck, 1979]*. However, this value will surely decrease with increasing distance from the river mouth because of preferential settling of heavy particles; indeed the lowest Ti / Al value in our samples (459) is below this river value. Assuming a Ti / Al ratio of 459 for the river end-member and 623 for the aeolian end-member in the Lido Rossello area, we can calculate the percentage aeolian input in the beige (86%), white (37%) and grey layers (13%). This implies that, compared with the white intervals, aeolian input is a factor 2.3 higher in the dryer beige interval, and fluviatile input is a factor 1.4 higher in the wetter grey intervals. These values strongly depend on the assumed Ti / Al ratios of the end-members. Applying our selected values for river and aeolian input to top sediment (Ti / Al = 530) in box core UM 42 located in the Ionian Sea yields a present-day wind input of 80%, which is consistent with sediment trap data for this area *[Rutten et al., submitted]*. Still, the actual Pliocene Ti / Al aeolian dust and river Ti / Al values may have been considerably different from the applied values. Therefore, these numbers only give an idea of the relative changes in fluviatile and aeolian input that may occur. The large differences between the grey, white and beige layers, however, suggest that the absolute amount of detrital input may have varied as well. Thus, dilution of carbonates by detrital material may have occurred, by aeolian input in beige, and by river input in grey layers. Evidence for such changes has also been inferred from palynological and grain size data *[De Visser et al., 1989]*, from clay mineral data *[Foucault and Mélières, 1995]*, and from strontium isotope data *[Blenkinsop et al., 1994]*. $\delta^{13}C_{org}$ values have also been used to determine the relative contributions of terrestrial and marine input *[Van Os et al., 1994]*, but this parameter cannot be used for these purposes in a simple and straightforward manner in eastern Mediterranean sediments *[Chapter 7]*.

The variations in total carbonate content observed in the sediments can be achieved by a 75% higher detrital flux in grey and beige compared with white intervals. Therefore, our estimated variations in detrital input may account for the lower total carbonate content in the beige layers, but not for the carbonate decrease in the grey intervals. Also, the variations in planktonic foraminiferal shell flux of more than 1,600 shells m^{-2} day^{-1} in beige and white layers to 200 shells m^{-2} day^{-1} in grey layers cannot be explained by dilution alone. As we already excluded productivity as the main cause for these variations, carbonate dissolution probably played a significant role as well.

Early diagenesis, redox levels and carbonate dissolution

Carbonate dissolution may be a factor contributing to the low carbonate contents and foraminiferal shell fluxes in the grey layers. The fact that foraminifera shells in these layers appear well preserved does not prove that dissolution did not occur: selective dissolution of microfossils is possible *[Einsele, 1982; De Lange et al., 1994]*. Also, the "clean" appearance of foraminifera in the grey layers compared with those in the beige and white layers which often have carbonate overgrowths, may indicate that shells were "etched" by acids in the organic-enriched layers, and that carbonate precipitated on shells in the organic-poor layers. Such processes may enhance the original differences in sedimentary carbonate content *[Einsele, 1982]* and contribute to the decoupling of foraminiferal shell flux and total carbonate content.

An indication that carbonate dissolution did in fact occur in the Lido Rossello and Punta di Maiata sediments comes from Sr / $CaCO_3$ peaks around some grey layers, the laminite, and the diatomite. Calcite contains about 0.14 wt% Sr, whereas aragonite, which is more soluble than calcite, contains ~ 1 wt% of this element *[Milliman, 1974]*. Carbonate dissolution, therefore, may result in mobilization of Sr, which can precipitate outside the zone of carbonate dissolution in Sr-rich carbonates, or as celestite ($SrSO_4$). Carbonates may be dissolved by acids released when organic matter is oxidized during diagenesis or weathering. In the grey layers, the diatomite, and the laminite, contents of redox-sensitive and chalcophilic trace elements as well as pyrite (inferred from Fe^* and S levels) are high, indicating that these layers have been formed under more oxygen-depleted conditions than the other sediments, and that sulphate reduction may have occurred during and after their deposition. During organic matter oxidation by sulphate reduction, bicarbonate addition causes supersaturation of calcite and aragonite *[Morse and Mackenzie, 1990]*. However, carbonate undersaturation occurs in the initial stages of sulphate reduction *[Canfield and Raiswell, 1991]*. Severe oxygen depletion and high levels of sulphate reduction during formation of the grey layers are unlikely because benthic foraminifera are present. Furthermore, bioturbation may have occasionally led to oxidation of pyrites and organic matter, producing additional acidity that may dissolve carbonates. The laminites, on the other hand, are devoid of benthos. Concluding, some carbonate may have dissolved during early diagenesis at least in the grey layers, but since pervasive sulphate reduction will result in carbonate supersaturation, this cannot have amounted to more than a few percent. Strontium mobilized by this mechanism may move outside the zone of sulphate reduction and precipitate when it encounters SO_4^{2-}, giving rise to celestite peaks *[Baker and Bloomer, 1988; Nijenhuis et al., 1996 (Chapter 2)]*. Alternatively, carbonate dissolution took place during subaerial weathering. In this case, organic matter is not oxidized by sulphate, but by oxygen, and carbonate supersaturation does not occur *[Canfield and Raiswell, 1991]*. Mobilized Sr may subsequently move outside the zone where carbonate is undersaturated, and precipitate as Sr-rich carbonate, also giving rise to Sr / $CaCO_3$ peaks.

A remarkable difference between the Lido Rossello and Punta di Maiata sections is the presence of much higher Sr / $CaCO_3$ peaks in the former (in fact, these peaks are so small in Punta di Maiata that they cannot be discerned in Fig. 4.3). In the Punta di Maiata section, the

(calculated) Sr content of carbonates gradually increases from 0.14 wt% at the bottom to 0.16 wt% at the top, without variation with lithology. This would imply an increase of aragonite in the carbonate-fraction from 0% at the bottom to 2% at the top of the section (assuming 0.14 wt% Sr in calcite; 1 wt% in aragonite). At Lido Rossello, the Sr content of carbonates is slightly higher, 0.17 wt% on average, increasing from 0.16 in the bottom to 0.19 wt% (or 6% aragonite in carbonates) at the top of the section. We can calculate the amount of Sr mobilized, the associated dissolved carbonate, and the original Sr / $CaCO_3$ value from the Sr peaks around, for example, the grey layer of cycle 30, assuming that the Sr / $CaCO_3$ peaks only result from carbonate dissolution in that layer. The amount of dissolved carbonate corresponding to the mobilized Sr depends on whether aragonite (containing 1 wt% Sr) or calcite (containing 0.14 wt% Sr) dissolved. If we assume that only aragonite dissolved from the grey layer, then the Sr quantity in the spikes represents 4% of the carbonate originally present in that layer. In this case, 8% aragonite must have been present in the initial grey layer. If we assume that only calcite dissolved, then the Sr quantity in the spikes represents 14% of the carbonate originally present in the grey layer, and 6% aragonite was initially present. Obviously, the real amount of carbonate that dissolved must lie somewhere between these two values. Dissolution of 10-14% of the carbonate initially present in the grey layer can account for the difference in carbonate content between the white and the grey layers; dissolution of 4-10% is insufficient but may have emphasized the differences between the grey and white layers. It may also account for the clean appearance of foraminifera in the grey layers and the overgrowths in the white intervals (precipitation of dissolved carbonate). Concluding, some grey layers were originally richer in aragonite, which subsequently dissolved when organic matter was oxidized by sulphate reduction or during diagenesis.

Sulphate reduction may result in barite dissolution *[e.g. De Lange et al., 1994]*. The M-shaped Ba^* profiles around the grey layers (Fig. 4.4) indicate that some Ba mobilization took place. The diatomite constitutes the only interval in these sediments where the C_{org} and Ba^* profiles are decoupled: in the upper part, highest C_{org} contents are reached whereas relatively little Ba is present, and in the lower part maximum Ba contents are accompanied by C_{org} contents only slightly higher than in the grey intervals. Barium may have migrated outside the upper part of the diatomite and precipitated in the lower part, enhancing the Ba productivity signal there. However, if sulphate reduction continued in the organic rich layer after deposition of younger, organic-poor strata, a mobilization peak would also be expected above the diatomite. Such a Ba spike is not found. Thus, the relatively low Ba content in the upper diatomite is probably not the result of barium mobilization. A comparison with the brown layer shows that the Ba and C_{org} of this layer are very similar to those of the upper diatomite. Perhaps then, it is not the Ba content of the upper diatomite that is relatively low, but that of the lower part that is relatively high. The highest opal contents also occur in the lower diatomite, and Ba may particularly be associated with diatoms *[Bishop, 1988]*. In anoxic hypersaline basins in the Mediterranean, bottom waters contain increased silica contents *[De Lange et al., 1990]*, and well-preserved opaline species are encountered *[Erba, 1991]*. During deposition of the diatomites,

the Lido Rossello area may have been similar to such an anoxic basin, where a build-up of silica concentration at times of high productivity resulted in preservation of diatoms and associated barium. Redox-sensitive trace elements are enriched in the lower diatomite, confirming stronger oxygen depletion. In the Lido Rossello section, up until the brown layer, the pyrite content is higher than at Punta di Maiata, indicating that sulphate reduction may have been more persistent in this interval. Additionally, there is a slump level directly below the first of the six diatomites *[Brolsma, 1978]*, possibly indicating the formation of a small basin. The presence of a depression at Lido Rossello may explain some of the features and the local occurrence of the diatomites, but it cannot account for all characteristics. For example, *Lourens et al. [in prep.]* showed that there are distinct changes in the water column characteristics at times of diatomite formation, which do not occur at Punta di Maiata. Also, it cannot be explained why the occurrence of diatomites is not restricted to a specific part of the cycles, e.g. only to the high productivity grey layers.

Weathering

Whereas variations of $\delta^{13}C_{org}$ with lithology are lacking in the grey-white-beige-white sequence, there is a distinct shift to lighter values in the lower, opal-rich part of the diatomite, and a shift to heavier values in the upper, C_{org}-rich part. The laminite in cycle 30 also shows heavier $\delta^{13}C_{org}$. These heavier values may result from a contribution of organic matter derived from diatoms, which is 3-4‰ heavier in $\delta^{13}C_{org}$ than dinoflagellate and coccolithophore organic matter *[Tyson, 1994]*. Additionally, planktonic archaea found in the laminite also have relatively heavy $\delta^{13}C_{org}$ values of around -20‰ *[Hoefs et al., 1997]*. The highest abundance of diatoms in the lower part of the diatomite is accompanied by lighter instead of heavier $\delta^{13}C_{org}$ values. Prasinophyceae are characterized by a particularly light $\delta^{13}C_{org}$ of -28.6‰ *[Prauss and Riegel, 1989]*, but these are present in similar quantities in the upper and lower part of the diatomite *[Lourens et al., in prep.]*. $\delta^{13}C_{org}$ is often interpreted in terms of marine / terrestrial input, and this would mean that the diatom-rich interval would be characterized by relatively more terrestrial organic matter. This is highly unlikely and fits in the pattern that this classic interpretation does not hold in the Mediterranean *[Chapter 7]*. An alternative interpretation is that the light values in the lower diatomite and the lower C_{org} contents are the result of organic matter oxidation during weathering. Oxidation after uplift might be stronger in this part because of better developed lamination, providing a pathway for fluids containing oxidants. A similar effect of weathering on $\delta^{13}C_{org}$ has been reported in a laminated part of the nearby Punta Piccola section *[Van Os et al., 1996]*. The light values at 4.634 and 4.678 Ma (Fig. 4.4) may also result from weathering in less fresh samples. If organic matter oxidation did indeed occur in the lower diatomite, Sr-mobilization peaks resulting from carbonate dissolution would be expected around this layer. A Sr / $CaCO_3$ peak is observed above this layer, but not below; since the upper Sr peak only consists of one sample, however, the lower peak may have been missed because of insufficient sample density (3-4 cm).

Conclusions

- Although Ba indicates that palaeoproductivity in the quadripartite cycles was highest in the grey layers, planktonic foraminiferal shell fluxes are higher in the white and beige layers. There is no direct evidence for an increase in diatom / radiolarian productivity in the grey layers.
- Ti / Al profiles indicate that significant changes in the relative contribution of aeolian and fluviatile detrital matter occurred. A 75% relative increase in detrital input in the grey and beige layers with respect to the white layers may explain the decrease in total carbonate content, but cannot account for the low shell flux in the grey layers.
- Carbonate dissolution occurred in some of the grey layers (4-14% of the carbonate initially present) and in the laminites, resulting in Sr / $CaCO_3$ peaks around these layers.
- There may have been a local depression at Lido Rossello during formation of the laminated intervals at Lido Rossello. Stagnant bottom water in such a basin can account for high opal and barium contents in these layers.