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Borna Lužar-Oberiter
University of Zagreb

Peter A. Hochuli
Universität Zürich

Ljubomir Babić
University of Zagreb

Bosiljka Glumac
Smith College, bglumac@smith.edu

Darko Tibljas
University of Zagreb

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Climatic cycles recorded in the Middle Eocene hemipelagites from a Dinaric foreland basin of Istria (Croatia)

BORNA LUŽAR-OBERITER[1], PETER A. HOCHULI[2], LJUBOMIR BABIĆ[1], BOSILJKA GLUMAC[3] and DARKO TIBLJAŠ[4]

[1]Institute of Geology and Paleontology, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia;
✉bluzar@geol.pmf.hr
[2]Paläontologisches Institut, Universität Zürich, Karl Schmid-Strasse 4, CH-8006 Zürich, Switzerland
[3]Department of Geosciences, Smith College, Northampton, Massachusetts 01063, USA
[4]Institute of Mineralogy and Petrology, Faculty of Science, University of Zagreb, Horvatovac 95, 10000 Zagreb, Croatia

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Abstract: Middle Eocene hemipelagic marls from the Pazin-Trieste Basin, a foreland basin of the Croatian Dinarides, display repetitive alternations of two types of marls with different resistance to weathering. This study focuses on the chemical composition, stable isotopes, and palynomorph content of these marls in order to better understand the nature of their cyclic deposition and to identify possible paleoenvironmental drivers responsible for their formation. The less resistant marls (LRM) have consistently lower carbonate content, lower $\delta^{18}O$ and $\delta^{13}C$ values, and more abundant dinoflagellate cysts than the more resistant marls (MRM). We interpret these differences between the two marl types to be a result of climatic variations, likely related to Milankovitch oscillations. Periods with wetter climate, associated with increased continental runoff, detrital and nutrient influx produced the LRM. Higher nutrient supply sparked higher dinoflagellate productivity during these times, while reduced salinity and stratification of the water column may have hampered the productivity of calcareous nannoplankton and/or planktonic foraminifera. In contrast, the MRM formed during dryer periods which favoured higher carbonate accumulation rates. This study provides new information about the sedimentary record of short-scale climate variations reflected in wet-dry cycles during an overall warm, greenhouse Earth.

Key words: Eocene, Dinarides, Croatia, climate, cycles, hemipelagites.

Introduction

Deep-sea pelagic and hemipelagic strata are perhaps the best recorders of cyclic climatic changes due to their largely uninterrupted depositional history with little or no local influences. These deposits commonly display small-scale alternations in lithology, which are usually interpreted as a product of cyclic climatic changes driven by orbital forcing (e.g. de Boer & Smith 1994; and references cited therein). Climatically driven changes in atmospheric and oceanographic conditions affect the productivity of organisms, influx of terrigenous material, as well as ocean circulation and oxygen concentrations. Consequently, small-scale sedimentary cycles of similar appearance can have variable origins as cycles of productivity, dissolution, dilution by terrigenous input, or redox cycles (Einsele 1982). Although any of these mechanisms can by itself produce cyclic lithological alternations, in a natural environment, it is often reasonable to assume that a complex interplay of these mechanisms is responsible. In some cases diagenesis is interpreted as generator of rhythmic bedding by causing carbonate redistribution. However, it is generally considered unlikely that diagenesis is capable of creating rhythms from initially homogeneous sediment by self-organization alone, but instead only enhances an already existing cyclic pattern (Einsele 1982; Böhm et al. 2003). An array of different analytical methods are commonly used to identify and distinguish between the possible causes of cyclic alternations, including

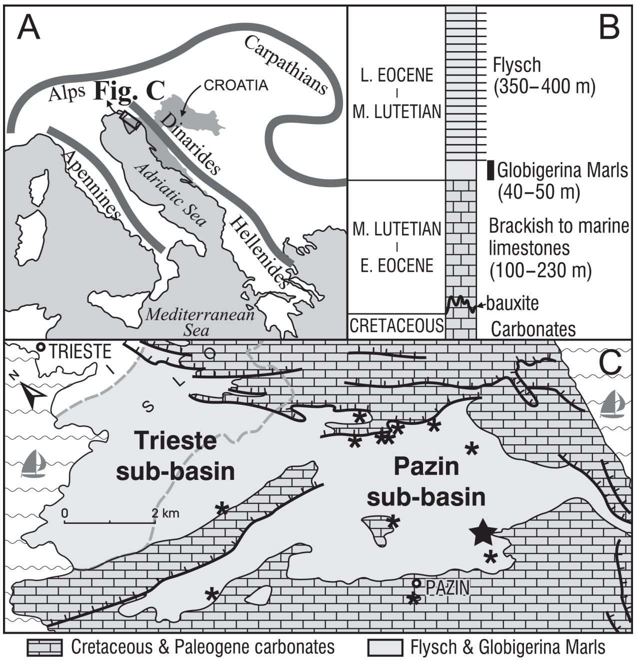

Fig. 1. Study area. **A** — Location of the study area (framed) within the Mediterranean region. **B** — Stratigraphic position of the investigated Globigerina Marls unit. **C** — Simplified geological map of the study area. Small stars mark the locations of outcrops of Globigerina Marls showing cyclicity. The large star is the location of the studied outcrop.

major and trace element geochemistry, stable isotopes, micro- and nannofossil records, and time series analysis (Schwarzacher 2000).

Although the most profound expression of orbital forcing on climate is the occurrence of ice ages (Hays et al. 1976), many examples of pre-Pleistocene cyclic successions demonstrate that orbital forcing may influence the sedimentary record in an ice-free greenhouse world (de Boer & Smith 1994). Orbitally driven cyclicity has been widely studied in pelagic and hemipelagic successions of different settings: oceanic domains, intermontane basins, grabens, and epicontinental settings (de Boer & Smith 1994; D'Argenio et al. 2004; and references cited therein). Here we describe small-scale cycles formed in a specific paleogeographic location and stage of peripheral foreland basin evolution. The cycles occur in the Middle Eocene hemipelagites from the Pazin-Trieste Basin on the Istrian peninsula of the coastal Croatian Dinarides (Fig. 1A–C; Lužar-Oberiter et al. 2004). Variations in chemical composition, stable isotopes, and palynomorph content have been investigated. These offer new insights into the nature of the cycles and the driving mechanisms responsible for their formation. They provide a new understanding of how climate influenced sedimentation in the foreland basin of the Dinaric region of Croatia during the Middle Eocene greenhouse climate.

Geological setting

The sedimentary cyclicity that this study focuses on is characteristic of hemipelagic marls which make up a lithostratigraphic unit named Globigerina Marls by Schubert (1905). This unit occupies a specific position in the sedimentary and tectonic evolution of the Pazin-Trieste Basin, an Eocene Dinaric foreland basin (Fig. 2A). The NW–SE elongated basin evolved on top of Mesozoic carbonates, which were first emerged and karstified, and subsequently overlain by a brackish to marine limestone succession of Early to Middle Eocene age (Fig. 1B; Schubert 1905; Muldini-Mamužić 1965; Drobne 1977). This succession is further overlain by the Upper Lutetian to Upper Eocene Globigerina Marls unit and flysch deposits (Muldini-Mamužić 1965; Kraseninnikov et al. 1968; Piccoli & Proto-Decima 1969). The Globigerina Marls unit of the Pazin-Trieste Basin is regarded as the middle member of the underfilled foreland trinity of Sinclair (1997), which follows the formation of a forebulge, and consists of ramp limestones, hemipelagites, and flysch (Fig. 2B; Živković & Babić 2003). The development of this tripartite succession was related to the subsidence of the foreland towards the SW in response to the load imposed by the propagating Dinaric tectonic structures from the NE. The onset of hemipelagic deposition marks the time when carbonate production could not keep pace with subsidence, while the sedimentation of the overlying flysch started when the area came under the influence of the orogen and received detritus from the orogen to the NE and from the carbonate foreland to the SW (Babić & Zupanič 1996). The abundance of planktonic foraminifera in the Globigerina Marls unit suggests deposition at depths of about 1000 m (Gohrbandt 1962; Juračić 1979; Živković & Babić 2003). The Globigerina Marls unit is a 40 to 60 meter thick monotonous succession of grey marls, homogeneous in appearance, exposed along the margins of the basin. Thin turbiditic layers are very rare, but become more common up-section at the transition to flysch. Subtle cyclicity is observable at many localities, but it is commonly obscured in tectonically disturbed areas and only well preserved in smaller segments of individual outcrops of the Globigerina Marls unit. Our detailed study was conducted in an outcrop located in the southern part of the basin (Figs. 1C, 3), where the strata display horizontal bedding and negligible tectonic disturbance. This part of the succession corresponds to the middle part of the unit, and has been assigned to the lower part of the planktonic foraminiferal Zone P12 of Berggren et al. (1995) (Živković & Babić 2003) which corresponds to Zone E10 of Berggren & Pearson (2005).

The studied cycles consist of two types of marls identified on weathered surfaces of certain outcrops: marls more resistant to weathering (MRM — sample numbers U) slightly protrude from the outcrop surface compared to less resistant marl (LRM — sample numbers L) intervals in between them (Fig. 3A). Transitions between the two marl types are always gradual. The subtle nature of the cyclicity does not allow visual identification in all outcrops of the Globigerina Marls unit. In the studied outcrop the average thickness of individual MRM–LRM couplets is approximately 35 cm, without much variation laterally and vertically.

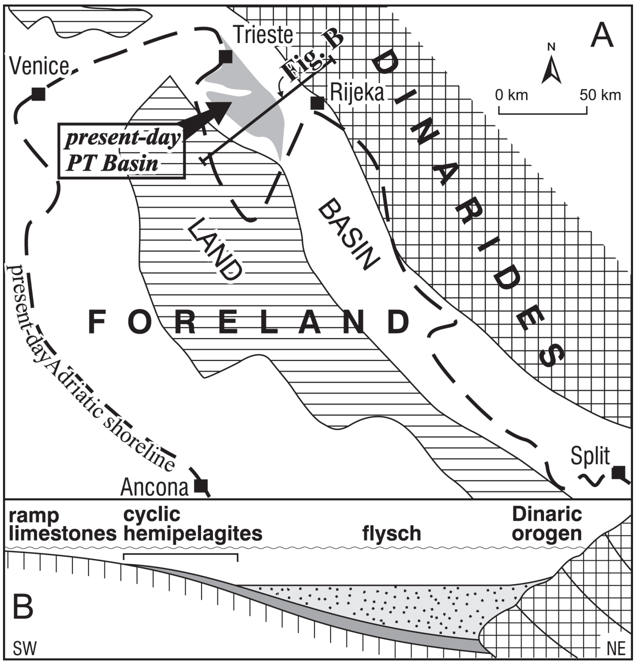

Fig. 2. Reconstruction of the Pazin-Trieste (PT) Basin. **A** — Paleogeographic map of the Adriatic region during the Lutetian showing the position of the PT Basin (after Tarlao et al. 2005). **B** — Cross-section through the basin showing its location in front of the advancing Dinaric orogen and the structural and depositional setting of the cyclic Globigerina Marls unit.

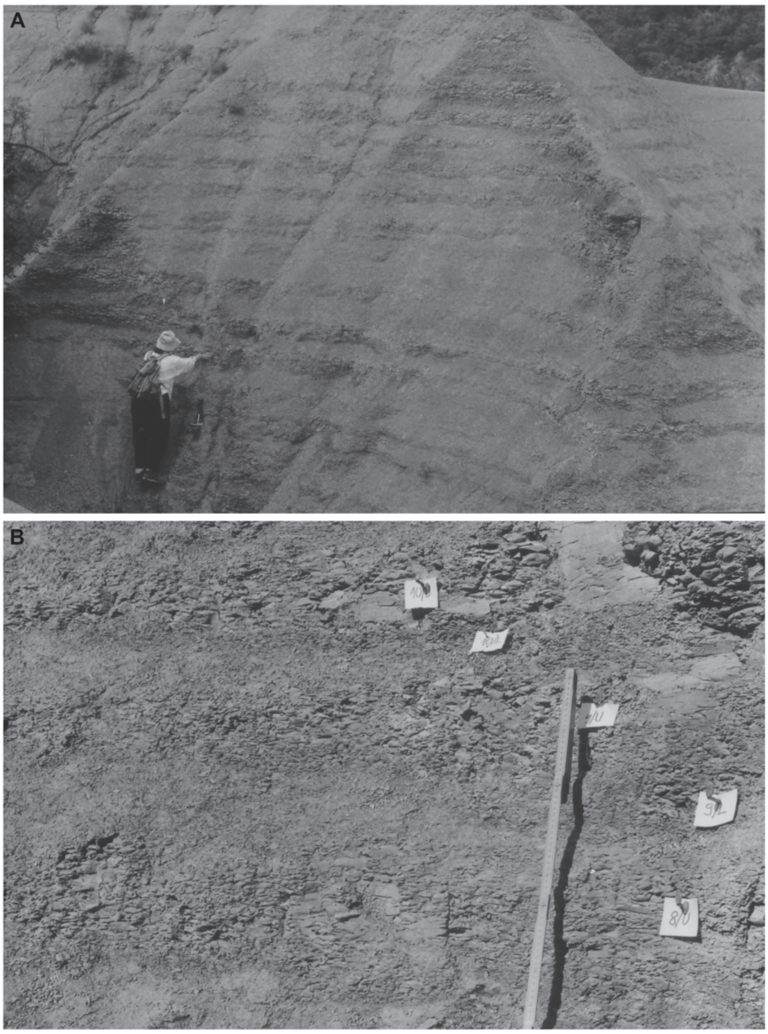

Fig. 3. Field photographs of the Globigerina Marls deposits of the Pazin Basin in Istria, Croatia. **A** — View of the studied outcrop with the clearly visible alternations of marls with slightly different resistance to weathering. **B** — Close up view of a segment of the studied outcrop during sampling. Positions of samples were marked prior to the removal of the weathered surface material.

Methods

Sampling points were chosen where the MRM and LRM could be most clearly differentiated in the outcrop. The position of each sample was marked before removing the weathered surface cover since the differentiation between the two marl types proved to be difficult after cleaning the rock surface (Fig. 3B). Several intervals in the studied section were omitted due to insufficient quality of the exposure (see Fig. 4).

Element concentrations were determined by ICP-MS. $CaCO_3$ contents were measured by complexometrical titration. XRD analyses on unoriented whole-rock mounts and scanning electron microscope imaging were used to identify the mineral constituents and refine the petrography of the marls. Organic carbon (C_{org}) was determined by combustion of dry, carbonate free samples on a LECO IR 212 instrument.

For stable isotope analysis whole-rock powdered samples were roasted at 380 °C for one hour to remove volatile contaminants. After reacting with 100% H_3PO_4 at 70 °C for 5 minutes they were analysed using an on-line automated carbonate preparation system (Kiell III) linked to a Finnigan-MAT DeltaXL+ ratio mass spectrometer. Standard isobaric and phosphoric acid fractionation corrections were applied to all results, and analytical precision was monitored through daily analysis of a variety of carbonate standards.

For palynological analysis cleaned, crushed and weighed samples (15 g) were treated with HCl and HF following standard preparation techniques (e.g. Traverse 2007). All samples were productive and were studied for their content of particulate organic matter and palynomorph types (e.g. phytoclasts, dinoflagellate cysts, acritarchs, and spore-pollen). A minimum of 250 particles were determined and counted per sample.

Results

Both the LRM and MRM consist of calcite, quartz, muscovite/illite, kaolinite and smectite. Only calcite and quartz show well defined peaks on the X-ray spectra. Observation under the scanning electron microscope showed no apparent difference between the two marl types. In all samples most of the carbonate is present as nannoplankton and foraminiferal remains, which are generally well preserved. Minute barite crystals occur mostly as scattered individual crystals and occasionally in small aggregates.

$CaCO_3$ content varies from 46.70 to 63.46 %, with samples from the LRM layers containing on average about 11 % less $CaCO_3$ compared to the MRM (Fig. 4). Measured bulk carbonate $\delta^{18}O$ values vary between −1.18 ‰ and −2.69 ‰. The MRM consistently have higher $\delta^{18}O$ values, averaging 0.86 ‰ above those of LRM (Fig. 4). The measured $\delta^{13}C$ values range between 0.69 and 0.91 ‰, and are higher in the MRM than in the adjacent LRM (Fig. 4). Both $\delta^{18}O$ and $\delta^{13}C$ values correlate positively with $CaCO_3$ content ($r^2=0.91$ and $r^2=0.71$, respectively; Fig. 5). SiO_2, Al_2O_3, TiO_2 and K_2O concentrations are higher in the LRM relative to the MRM. Al_2O_3 concentrations are positively correlated with concentrations of TiO_2, K_2O, and SiO_2, whereas concentrations of Al_2O_3 and CaO correlate negatively. C_{org} values are low for all the studied samples (0.10–0.15 %), and are slightly higher in the LRM (Fig. 4).

The preservation of palynomorphs is fairly good to excellent. Individual grains exhibit no obvious signs of post-depositional degradation. Thermally unaltered conditions of the organic matter are indicated by the virtually unchanged colour of the palynomorphs (thermal alteration index <2). In most samples the assemblages of particulate organic matter (POM) are strongly dominated by translucent phytoclasts,

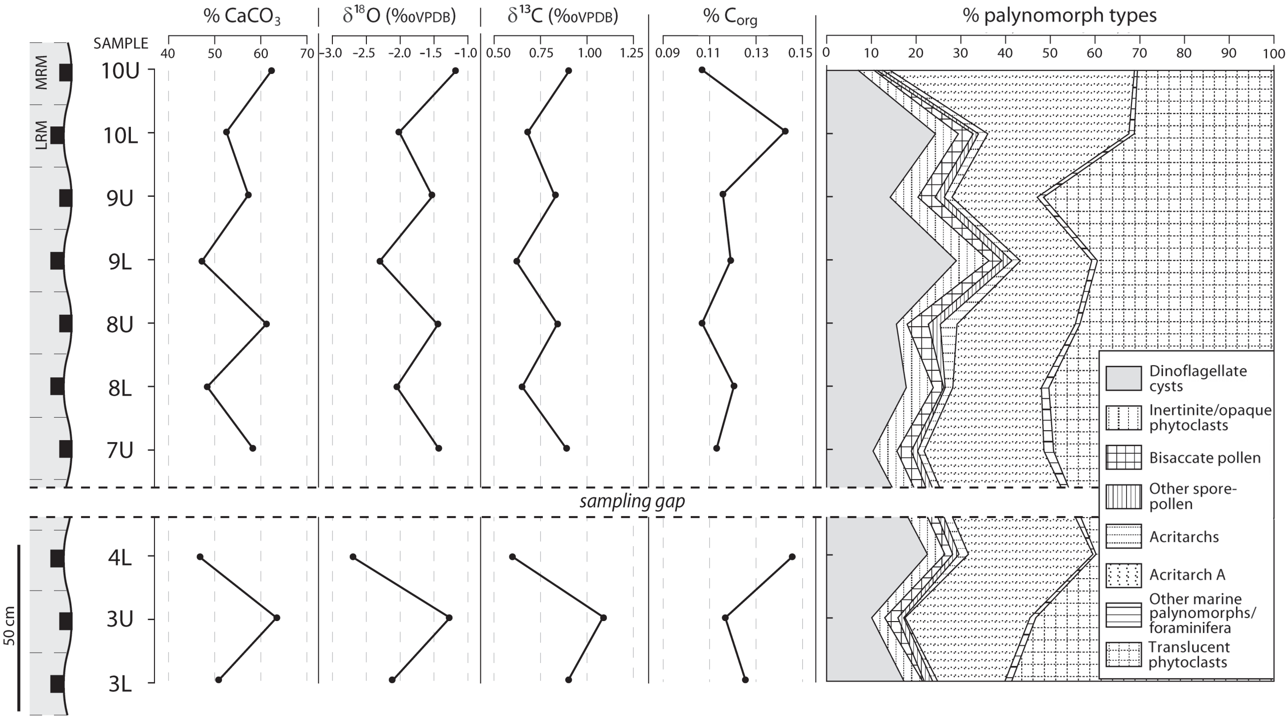

Fig. 4. Vertical variations in measured parameters within the studied section of the Globigerina Marls unit. Note the consistent differences in carbonate content, stable isotopes, dinoflagellate abundance, and C_{org} between the alternating less resistant (LRM; samples L) and more resistant (MRM; samples U) marls. The sampling gap is due to poor outcrop conditions.

including woody particles, and cuticles of terrestrial origin as well as membranes of undetermined origin. The second most abundant element is a particular type of acritarch (Acritarch A), which is characterized by a dense cover of long hair-like processes. Dinoflagellate cysts are also very common, representing the third most important POM constituent. All other groups including inertinite, opaque phytoclasts and the palynomorph groups such as acritarchs, bisaccate pollen and other spore-pollen grains, are present, but are quantitatively of minor importance. Among the various categories of palynomorphs, only dinoflagellate cysts seem to show a clear cyclic distribution. They are more common in the LRM (L samples in Fig. 4) than in the MRM.

Among the observed palynomorphs, dinoflagellate cysts are not only the most abundant component, but also show a relatively high diversity (see Appendix). The assemblages show a rather homogeneous composition throughout the studied interval. Compared to other coeval assemblages, some of the typical species of this stratigraphic interval (e.g. *Aerosphaeridium diktyoplokus* and marker species of the *Wetzeliella* group), have not been found in the studied samples. Pollen grains and spores are relatively rare. The spore-

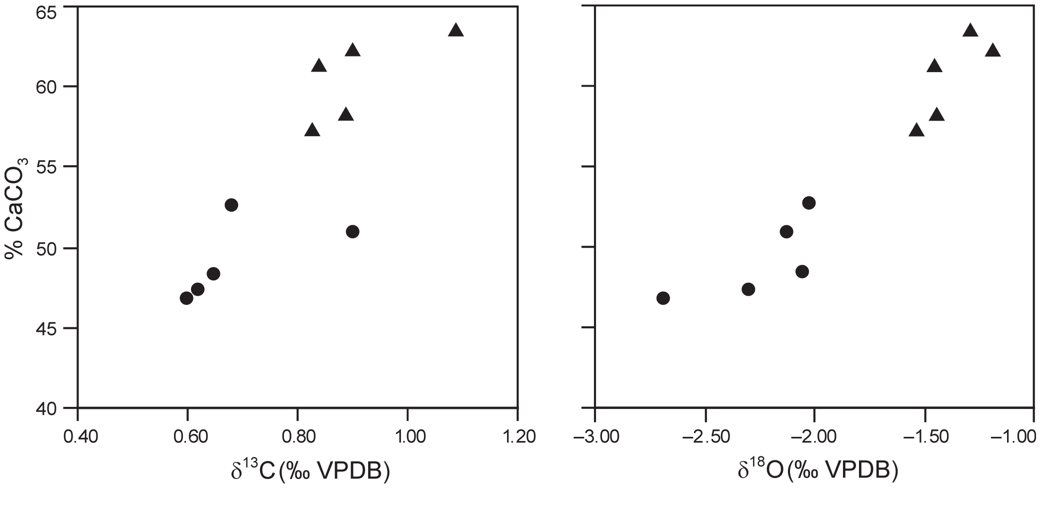

Fig. 5. Scatter plots showing the relationship between carbonate content and stable isotopes. A positive correlation is evident in both diagrams. Circles — LRM; triangles — MRM.

pollen assemblages are dominated by bisaccate pollen grains. Among the relatively rare angiosperm pollen, a few grains of *Echimonocolpites (Nipa)* were observed.

Discussion

Our geochemical and palynological data (Fig. 4) follow a cyclic pattern of deposition which corresponds to the vertical changes in the degree of weathering observed on the studied outcrop (Fig. 3). The parameters we have measured are generally considered to be good proxies for past environmental conditions (e.g. Pross & Schmeidl 2002; Mader et al. 2004; Sagasti 2005), which suggests that the deposition of the studied marls was influenced by cyclic changes in oceanographic conditions of the Eocene seaway which flanked the early Dinarides (Fig. 2).

Although commonly used as indicators of oceanographic conditions such as temperature, salinity and productivity, oxygen and carbon stable isotopes can be subject to serious diagenetic alterations, often causing difficulties in differentiating between a diagenetic and environmental signal (Mitchell et al. 1997). In the data from the studied marls, the correlation between $CaCO_3$, $\delta^{18}O$ and $\delta^{13}C$ (Fig. 5) is suggestive of a possible diagenetic imprint. However, if diagenetic carbonate reorganization was the cause of the approximately 11% difference in $CaCO_3$ between LRM and MRM, one would expect MRM to display more negative $\delta^{18}O$ values due to higher amounts of secondary carbonate cement (Thierstein & Roth 1991; Frank et al. 1999; Westphal 2006). The subtle and consistent differences in isotope values (Fig. 4), the overall good preservation of microfossils (Živković & Babić 2003; Živković & Glumac 2007) and the lack of a significant amount of secondary carbonate in the studied marls suggest the absence of notable diagenetic overprint. High clay content of both studied marl types would have prevented serious vertical circulation of porewater, creating a relatively closed diagenetic system. This contrasts with limestone–marl systems where carbonate ooze intervals, due to higher permeability and a greater number of carbonate growth centers, take on a larger amount of diagenetic carbonate (Mitchell et al. 1997; Frank et al. 1999). Although some postdepositional alteration of isotope values in both marl types cannot be ruled out, it is not probable that the observed relative differences in isotope values between LRM and MRM are purely a product of carbonate reorganization. Instead, it is probable that these differences reflect changes in oceanographic conditions.

We suggest that the deposition of the investigated marls was influenced by changes between wetter and dryer periods (Mader et al. 2004; Sagasti 2005). The positive correlation between $\delta^{18}O$ and $\delta^{13}C$ values suggests that variations in continental runoff, which can affect both isotopes, played a role in the formation of the observed cycles (Mader et al. 2004). During wetter periods, greater input from continental runoff led to an increased input of lighter isotopes, river fed nutrients and/or detrital siliciclastic material resulting in the formation of LRM (Fig. 6). The abundance of *Braarudosphaera* in the nannoplankton assemblages from the base of the Globigerina Marls unit has been suggested as an indicator of freshwater influx to the Pazin-Trieste Basin (Pavlovec & Pavšič 1986), and abundant vegetation rafted dropstones found in the basal parts of the Globigerina Marls point to the existence of deltaic systems located along the NE margin of the basin (Tarlao et al. 2005). The higher concentrations of Al_2O_3, TiO_2, SiO_2 and K_2O in the LRM samples, as well as their negative correlation with CaO, possibly reflect an increased siliciclastic terrigenous input for the LRM compared to the MRM. The sediment source area was the emerging Dinaric orogen to the NE, which later became an even more active source area for flysch deposits. However, dilution by changing terrigenous supply of detritus probably had a minor role in producing the marl cycles, as one would expect a larger thickness of LRM intervals (Einsele 1982). The higher abundance of dinoflagellate cysts in the LRM (Fig. 4) can be interpreted as a response to the increased influx of nutrients related to enhanced runoff. As no corresponding variation is observed in the distribution of POM of terrestrial origin, the similar trend in the C_{org} and dinoflagellate cyst abundance suggests that the differences in the abundance of dinoflagellate cysts between the LRM and MRM are related to changes in dinoflagellate productivity rather than changing input of terrestrial organic matter. At the same time overall productivity of calcareous nannoplankton and/or planktonic foraminifera was reduced as indicated by lower $CaCO_3$ concentrations and $\delta^{13}C$ values (Fig. 4). The cause of this may have been unfavourable oceanographic conditions due to a decrease in surface water salinity and possible stratification of the water column. In contrast to periods of wetter climate, during deposition of MRM the climate was less humid resulting in reduced continental runoff and possibly increased evaporation as suggested by higher $\delta^{18}O$ values. The waters of the Pazin Basin at these times experienced less stratification and conditions more suitable for calcareous nannoplankton and/or planktonic foraminifera which resulted in higher carbonate accumulation rates (Fig. 6). Changing paleoceanographic conditions have been reported from the same section of the Globigerina Marls unit by Živković & Glumac (2007), based on assemblages of small benthic foraminifera. Although they used much broader sampling intervals, these authors did

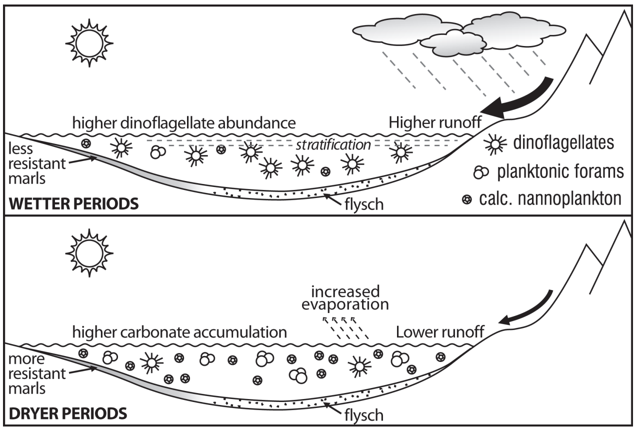

Fig. 6. Climatic and environmental conditions responsible for the origin of cyclicity in the Globigerina Marls unit of the Pazin-Trieste Basin during the Middle Eocene. See text for explanation.

identify episodes of higher refractory organic matter flux and/or lowered oxygen concentrations in the bottom waters during overall mesotrophic conditions.

During the Eocene, the region of Istria was situated in mid latitudes and experienced overall warm subtropical climate conditions (Pavlovec & Pavšić 1986; Živković & Babić 2003; Tarlao et al. 2005). The occurrence in the studied marls of *Echimonocolpites*, which is attributed to the mangrove palm genus *Nypa*, is typical of the Middle Eocene assemblages and is considered a good indicator of the optimum climatic conditions during the Eocene. Assuming similar climatic conditions for the fossil representatives of the genus as for the extant species, surface water temperatures would have been above 20 °C (Fechner 1988; Akkiraz et al. 2006).

In their modelling of Eocene greenhouse climate, Sloan & Huber (2001) showed that ocean-related climate processes responded significantly to variations in orbital forcing on a precessional scale (~21 ka), enough to produce rhythmic sedimentation in many regions of the world (e.g. D'Argenio et al. 1998; Burgess et al. 2008; Machlus et al. 2008). Cyclic changes in ocean surface moisture and continental runoff amounts were particularly pronounced in low latitudes. These changes were related to periods of higher and lower insolation and seasonality, which affected the intensity of monsoonal circulation in the atmosphere and associated precipitation patterns (Prell & Kutzbach 1992). The results of our study suggest that such Milankovitch-scale changes probably also had an influence on the mid latitude area of the Dinarides and caused shifts between wetter and dryer climatic periods during the Middle Eocene greenhouse climate. These climate changes are reflected in fluctuating amounts of biogenic and detrital material being supplied to the sediments of the Pazin-Trieste foreland basin (Fig. 6). This study illustrates how subtle small-scale depositional cycles, not always apparent and commonly obscured in the field, can become evident when examined in detail for their geochemistry and fossil content, and are able to provide unique insights into climatic oscillations. Such integrative data derived from sedimentary records are valuable and necessary inputs for various climate modelling efforts and for our ability to evaluate and predict complex temperature and precipitation patterns in an overall warm, ice-free world.

Conclusions

The regular alternations between less and more resistant marls observed in the Middle Eocene hemipelagic Globigerina Marls unit probably resulted from cyclic climatic changes between wetter and dryer periods affecting the mid-latitude Pazin-Trieste foreland basin of the Croatian Dinaric region. Our data suggest that periods of wetter climate, associated with increased continental runoff supplied by rivers draining the Dinarides along the NE margin of the basin, and ensuing higher detrital and nutrient influx, produced the LRM. An increased nutrient supply due to higher runoff may have been the cause for increased dinoflagellate productivity, but the reduced salinity as well as possible stratification of the water column reduced the overall productivity of calcareous nannoplankton and/or planktonic foraminifera. As a result, the LRM exhibit lower $\delta^{18}O$ and $\delta^{13}C$ values, lower $CaCO_3$, higher concentrations of SiO_2, Al_2O_3, TiO_2, K_2O and C_{org}, and higher abundance of dinoflagellate cysts compared to the MRM, which formed during periods of dryer climate. The dryer periods were in turn characterized by less runoff, higher salinity of surface waters and less stratification of the water column which favoured higher carbonate accumulation rates. This multifaceted study of depositional cycles in the Globigerina Marls unit of the Pazin-Trieste Basin provides important new data towards our understanding of short-scale climate variations reflected in wet-dry cycles, which were likely related to Milankovitch oscillations during the Eocene greenhouse Earth.

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Appendix

List of identified palynomorphs in the samples of the hemipelagic Globigerina Marls

***Dinoflagellate cysts*:**

Achilleodinium biformoides (Eisenack) — Eaton 1976
Achomosphaera alcicornu (Eisenack) — Davey & Williams 1966
Achomosphaera spp.
Caligodinium amiculum — Drugg 1970
Cerebrocysta spp.
Cordosphaeridium inodes (Klimpp) — Eisenack 1963
Cribroperidinium sp.
Dapsilidinium pastielsii (Davey & Williams) — Bujak et al. 1980
Deflandrea phosphoritica — Eisenack 1938
Diphyes colligerum (Deflandre & Cookson) — Cookson 1965
Distatodinium craterum — Eaton 1976
Distatodinium ellipticum (Cookson) — Eaton 1976
Enneadoysta arcuata (Eaton) — Stover & Williams 1995
Glaphyrocysta sp.
Heteraulacacysta leptalea — Eaton 1976
Histiocysta spp.
Homotryblium plectilum — Drugg & Loeblich Jr. 1967
Homotryblium tenuispinosum — Davey & Williams 1966
Hystrichokolpoma cinctum — Klumpp 1953
Hystrichokolpoma rigaudiae — Deflandre & Cookson 1955
Hystrichostrogylon membraniphorum — Agelopoulos 1964
Hystrichostrogylon spp.
Impagidinium spp.
Lejeunecysta spp.
Lentinia serrata Bujak — Bujak et al. 1980
Lingulodinium machaerophorum (Deflandre & Cookson) — Wall 1967
Melitasphaeridium pseudorecurvatum (Morgenroth) Bujak — Bujak et al. 1980
Operculodinium microtriainum (Klumpp) — Islam 1983
Operculodinium spp.
Phthanoperidinium echinatum — Eaton 1976
Rottnestia borussica (Eisenack) — Cookson & Eisenack 1961
Samlandia chlamydophora — Eisenack 1954
Spiniferella cornuta (Gerlach) — Stover & Hardenbol 1994
Spiniferites ramosus (Ehrenberg) — Mantell 1854
Spiniferites spp.
Thalassiphora pelagica (Eisenack) — Eisenack & Gocht 1960
Wetzeliella aff. *spinulosa* — Wilson 1988

***Acritarchs*:**

Comasphaeridium sp.
Acritarch sp. A (hairy) "*Kalyptocysta exoleta*" Stover

***Spore-pollen*:**

Bisaccate pollen (common, partly reworked)
Cicatricosisporites dorogensis — Potonié & Gelletich 1933 (consistent)
Classopollis spp. (rare, reworked)
Echimonocolpites spp. (Nypa, rare)
Podocarpidites spp.
Polypodiaceoisporites spp.
Trilites multivallatus (Pflug) — Krutzsch 1959