Astrochronology of the Mediterranean Langhian between 15.29 and 14.17 Ma

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A B S T R A C T

An integrated high-resolution magnetobiocyclostratigraphy including radioisotopic dating and astronomical tuning is presented for the interval between 15.29 and 14.17 Ma in the marine La Vedova section in northern Italy. The natural remanent magnetization is carried by the iron sulphide greigite and the resultant magnetostratigraphy can be correlated straightforwardly to the interval ranging from C58n.2n to C5ADn in the Astronomically Tuned Neogene Time Scale (ATNTS2004). Spectral analysis on high-resolution magnetic susceptibility and geochemical proxy records in the depth domain and, using our magnetostratigraphic age model, in the time domain demonstrate that the various scales of cyclicity in the section are related to astronomical climate forcing. Starting from our initial age model, larger-scale cycles were first tuned to eccentricity. This first-order tuning was followed by tuning the basic cycle to precession and boreal summer insolation using inferred phase relations between maxima in Ca/Al, redox-sensitive elements and Ba, and minima in magnetic susceptibility, and maxima in precession and minima in obliquity and boreal summer insolation. Our astronomical ages for reversal boundaries are supported by analysis of sea floor spreading rates and should replace the existing ages in the ATNTS2004 lacking direct astronomical control. Two major steps in the geochemical proxy records, astronomically dated at 15.074 and 14.489 Ma, coincide with abrupt changes in sedimentation rate, and are the result of the combined effect of the ~400-kyr eccentricity cycle superimposed upon a longer-term climatic or tectonic induced trend.

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1. Introduction

The accuracy, precision and resolution of the geological time scale for the Neogene have improved considerably over the last decades, using an integrated stratigraphic approach combined with astronomical tuning. In the ATNTS2004 (Lourens et al., 2004), direct astronomical ages for chron boundaries are only available back to ~13 Ma based on the tuning of marine successions from the Mediterranean and open ocean. Reversal ages for the interval between 13 and 23 Ma were calculated from anomaly profiles of spreading distances along the Australian–Antarctic plate pair, in combination with limited astronomical control. Recently, direct astronomical ages have been published for all reversal boundaries in the interval between 16 and 24 Ma (Billups et al., 2004). As a consequence astronomical ages of magnetic reversals are, at present, only lacking for the interval between 13 and 16 Ma.

In the Mediterranean suitable marine sections that cover this gap are scarce. The La Vedova section in northern Italy is one of the most complete and continuous sections that cover part of this interval (Montanari et al., 1997). An ⁴⁰Ar/³⁹Ar age of 14.9±0.2 Ma for the “Aldo Level” provided the first independent dating of La Vedova (Mader et al., 2001, 2004). Subsequent Fourier analysis on stable isotopes, magnetic susceptibility and geochemical proxy records of an interval covering ~340 kyr suggested orbital forcing of the cyclicity and resulted in a preliminary astronomical tuning for the interval between 14.7 and 15.1 Ma (Mader et al., 2004).

In this paper, we will present an integrated (magnetobiocyclo-) stratigraphy including radioisotopic dating of ash layers and astronomical tuning of the La Vedova section. The tuning will provide new astronomical ages for biot stratigraphic events and reversal boundaries. Geochemical records are used for the identification and characterization of the sedimentary cycles. In turn, the resulting age model will be applied to reconstruct the palaeoclimatic and environmental history in the La Vedova section.

2. Geological setting and section

The predominantly marine marl–limestone sedimentation in the Umbria–Marche region was only interrupted by siliciclastic deposits...
in Pliocene times, related to the NE-advancing orogenic front (Montanari et al., 1997; Mader et al., 2004). The Miocene part is exposed in the cliffs between Ancona and Il Trave along the Adriatic coast (Fig. 1) and includes the Aquitanian to Langhian Bisciaro Formation, the Langhian to Tortonian Schlier Formation, the Messinian Euxinic Shale, and the Gessoso Soliferia Formation. The Schlier Formation is subdivided into three informal lithostratigraphic members, namely the massive, calcareous and marly member. The La Vedova section covers part of the calcareous member of Langhian age (Montanari et al., 1997) and is well exposed along the beach (Fig. 1a and b). Unfortunately the stratigraphic interval up to the base of the younger Monte dei Corvi section (Hüsing et al., 2007) is incomplete due to the presence of a landslide (Fig. 1a). However, the section can be extended high in the cliffs (Anja Mouriik, pers. comm.). This section, named La Vedova High Cliff, will be subject of a separate study but the basal part (2 m) has been included in the present study to pinpoint the next younger magnetic reversal.

3. Lithostratigraphy

The Langhian succession at La Vedova is characterized by an alternation of homogeneous dark marls and indurated homogenous marly limestones (Fig. 2). Following cleaning, the fresh coloured sediments can be visually distinguished into whitish, greyish or bluish limestones and greyish, brownish, bluish or greenish marls. The lower 10 m of the section is characterized by a rhythmic alternation of grey to brownish marls and white or bluish indurated limestones. Above 10 m, the brownish marls are replaced by grey or greenish marls that alternate with whitish or bluish indurated limestones. In the stratigraphic interval between 10 and 22 m, the thickness of both the marl and limestone beds is reduced. Within this interval, two intervals (9–12 m and 19–22.5 m) are dominated by relatively thin-bedded whitish or bluish limestones that are generally more indurated. At 22 m, the thickness of limestone and marl beds increases drastically and is similar to that in the lower 10 m of the section. In the upper 18 m (22–38 m), thick and indurated limestones rhythmically alternate with thin and less-indurated limestones, with grey to bluish marl intercalated regularly in between limestone beds. Prominent dark green marls occur in bundles of two or three at ∼14, ∼17, and 24 m. In total 6 ash layers are found in the section, including the previously dated Aldo Level.

Oriented cores were taken every 10 cm for palaeomagnetic purposes and additional (non-oriented) samples were collected between these levels for susceptibility measurements, and geochemical and biostratigraphic purposes. Each core has a diameter of 2.5 cm.

4. Geochemical and magnetic proxies

4.1. Geochemical proxy record

558 samples collected about every 5 cm were dried, crushed, and powdered to homogenize each sample with the aim of minimizing the effect of bioturbation. 125 mg was subsequently dissolved in 2.5 ml HF (40%) and 2.5 ml mixing acid (HNO₃ 16.25% and HClO₄ 45.5%) and heated at 90 °C in a closed vial for at least 8 h. Samples were then dried by evaporating the acids at 160 °C and subsequently dissolved in 25 ml HNO₃ (4.5%). The resulting solutions were analyzed for major elements by a Perkin Elmer Optima 3000 ICP-OES at Utrecht University. Based on the general assumption that all Ca is derived from (calcium) carbonate, CaCO₃ is calculated by multiplying measured Ca values by 2.496. This yields CaCO₃ contents between 30% and 90%.

Fig. 1. (a) Location and sample trajectory of the La Vedova section (thick line along the coast) north of the younger Monte dei Corvi section, northern Italy. Note the landslide covering the interval between these two sections. Asterisk indicates location (adapted from Hüsing et al. (2007)). (b) and (c) Photographs showing the here presented La Vedova section and the exposure of the Monte dei Corvi along the beach.
All geochemical proxies reveal large- and small-scale variations, but also some discrete steps. We therefore subdivided the section into three intervals (I, II and III) with the boundaries corresponding to the major changes in lithology and sedimentation rate (Fig. 2). Each interval is characterized by distinct trends on which high-frequency variations are superimposed.

Interval I (0–9.5 m) is generally characterized by high Ba, V and S contents. This reflects the high organic content of the grey and in particular of the brownish marls. The top is marked by a sudden drop in Ba/Al and S/Al and decreased values in V/Al at ~8.5 m. CaCO$_3$ content generally increases through this interval and correlates negatively with magnetic susceptibility. Interval II (9.5–22 m) is characterized by small-scale and larger-scale fluctuations in all elements, which are particularly obvious in magnetic susceptibility, CaCO$_3$, V/Al, Ti/Al, and Zr/Al. Ba and V, the latter a redox-sensitive element, are positively correlated and show a strong anti-correlation with magnetic susceptibility. Long-term variations in CaCO$_3$ are generally positively correlated with V/Al and negatively with Zr/Al. The top of this interval is characterized by a sharp decrease in CaCO$_3$ content and a second, less obvious, drop in Ba/Al and S/Al. In interval III (22–38 m), mean Ba/Al and S/Al values remain relatively constant and show low amplitude changes. Peaks in Ti/Al generally occur a few centimeters above CaCO$_3$ peaks. In the long-term trend, Ti/Al and CaCO$_3$ are negatively correlated.

4.2. Magnetic susceptibility

The magnetic susceptibility of 300 samples has been measured on a Kappabridge KLY-2. Measured susceptibility values were divided by the sample's weight, yielding the specific susceptibility, given in $10^{-7}$ m$^3$/kg. In general, the specific magnetic susceptibility is relatively low, ranging from 1.01 to 6.15 $10^{-7}$ m$^3$/kg (Fig. 2). The highest values are generally found in marls, whereas limestones are characterized by low values. Plotting the magnetic susceptibility in stratigraphic order reveals a general decrease in values from 0 to 22 m, followed by a sudden increase in the interval between 22 and 38 m. Relatively large and regular variations with a recurrence of 0.6 to 1.2 m are present throughout the section.

5. Calcareous plankton biostratigraphy

5.1. Material and methods

A semi-quantitative analysis of selected plankton foraminifer taxa was carried out on 51 samples, taken generally from the marly layers of the sedimentary cycles, while the semi-quantitative distribution of Paragloborotalia siakensis is based on 156 samples. Preservation of planktonic foraminifera varies from moderate to poor. Counting was made on splits of the greater than 125 µm fraction of the washed residue, and is based on the number of a specific taxon in nine fields with a maximum of 30 specimens, using a rectangular picking tray of 45 fields. In case of abundant taxa, all the specimens present in the first field were counted even when exceeding 30 individuals. In addition, 66 samples were studied for calcareous nannofossil biostratigraphy. The analyses were performed with a polarized light microscope, at 1250× magnification, on smear slides prepared following standard methodology (Bown, 1998). A qualitative analysis was carried out on the assemblages in terms of abundance and preservation, whereas a quantitative analysis was performed on the genera Sphenolithus and Helicosphaera following Backman and Shackleton (1983) and Rio et al. (1990). More specifically, countings of 30–50 sphenoliths and of 50–100 helicotholiths were performed to evaluate the abundances of S. heteromorphus and H. waltrans species, respectively.

5.2. Results

The biostratigraphic analysis based on planktonic foraminifera focused not only on the main events (i.e. evolutionary stages of Praeorbulina/Orbulina lineage), which define zonal boundaries in the Langhian interval, but also on additional faunal changes having a biostratigraphic significance in the Mediterranean (Abdul Aziz et al., 2008; Di Stefano et al., 2008). The genera Praeorbulina and Orbulina show a discontinuous distribution pattern and are generally rare (Fig. 3). On the basis of the available data and the combined effects of the discontinuous distribution and rarity of the individual species, the scattered occurrence of transitional specimens between successive stages of the Praeorbulina/Orbulina lineage and the non-optimal preservation, the First Occurrences (FOs) of P. glomerosa glomerosa, P. glomerosa circularis, O. suturalis and O. universa cannot be accurately defined (Fig. 3). The uncertain definition of the latter three events hampered an accurate placement of the base of the MMI4d, MMI5a and MMI5b Subzones of Di Stefano et al. (2008). Additional faunal changes, as an influx of Globoquadrina dehiscens and an Acme interval of P. siakensis, are more clearly recorded. G. dehiscens is commonly and rather continuously present between 8 and 12 m, and is associated with an interval of common Globigerinoides subquadratus and Catapsydrax parvus while the Globorotalia praesculita gr. is nearly absent (Fig. 3). The G. dehiscens influx is followed by an Acme interval of sinitrally coiled P. siakensis, between 13 and 36 m, which is characterized by strong fluctuations and some marked drops in abundance (around 14 m, and between 15–16, 18–19, and 32–33 m). The P. siakensis Acme interval is associated with the first occurrences of O. suturalis and O. universa and corresponds to the Acme b Interval defined in other Mediterranean records by Di Stefano et al. (2008). Calcareous nannofossil assemblages are dominated by the genera Coccolithus, Cyclicocarolitius and Ditycococites. Also Helicosphaera and Sphenolithus are well represented, while Discoaster is less common or rare. S. heteromorphus generally shows very high percentages, except for a few samples in the lowest 4 m where it is nearly absent. The near absence of S. heteromorphus is likely due to dissolution effects since these levels are characterized by very rare sphenoliths and numerous more resistant discoasterids. Accordingly, the base of the section postdates the Paracme End of S. heteromorphus. This interpretation is supported by the absence of an Acme interval of randomly coiled P. siakensis, indicated as Acme by Di Stefano et al. (2008) and Abdul Aziz et al. (2008), which approximates the S. heteromorphus Paracme End. Helicosphaera waltransensis shows a discontinuous distribution pattern with abundances generally not exceeding 10%. H. waltrans is rare and discontinuously presents up to 25.29 m, where its Last Common Occurrence (LCO) is preliminarily placed. In terms of calcarceous nannofossil biozones, the La Vedova section encompasses a stratigraphic interval that falls between the end of the S. heteromorphus Paracme interval and the First Common Occurrence (FCO) of H. waltransensis corresponding to the MN5a and MN5b subzones of Di Stefano et al. (2008). The MN5a/MN5b boundary is defined by the H. waltrans LCO.

6. Palaeomagnetism

Oriented samples were taken for palaeomagnetic purposes about every 10 cm. A previous study to identify the nature of the remanence carrier in the nearby Monte dei Corvi section showed that isothermal remanent magnetization (IRM) acquisition curves provided the most valuable information (Hüsing et al., 2009). Hence, we carried out the same rock magnetic experiments on samples from La Vedova following the protocols of Hüsing et al. (2007, 2009).
6.1. Rock magnetism: IRM acquisition

All IRM acquisition curves were subjected to component analysis of cumulative log-Gaussian (CLG) curves (Kruiver et al., 2001). Every IRM curve was decomposed into a number of CLG curves, which can be individually characterized by their saturation IRM (SIRM), remanent acquisition coercive force ($B_{1/2}$), and dispersion parameter (DP).

IRM acquisition curves from La Vedova show four different components similar to samples from Monte dei Corvi. Component 1, introduced in the low field interval (Fig. 4a and supplementary Table 1), is interpreted as thermal activation and is therefore physically meaningless (Egli, 2004a,b; Heslop et al., 2004; Hüsing et al., 2009). Components 2 and 3 are both introduced between 42 and 62 mT, whereby Component 3 has generally lower $B_{1/2}$ values (42 to 45 mT) and a larger distribution parameter (DP). Both components are interpreted as greigite (e.g. Roberts, 1995; Horng et al., 1998; Vasiliev et al., 2007, 2008). The narrow grain size distribution and the high $B_{1/2}$ value of greigite Component 2 is indicative of a single domain (SD) particle size typical for a magnetotactic origin of greigite (Vasiliev et al., 2008) and is interpreted as syn-depositionally formed greigite (Hüsing et al., 2009). Component 3 has a larger DP ($\sim 0.36$), indicating a wider range of particle sizes, typical for authigenic (bacterially mediated) greigite that formed slightly later during post-depositional sulphidization processes. NRM acquisition of this greigite component can therefore be delayed (Hüsing et al., 2009).

Component 4 is introduced in the high field interval ($B_{1/2}$ between 200 and 400 mT and DP of $\sim 0.3$; supplementary Table 1) and is interpreted as goethite (Hüsing et al., 2009), which is likely a product of weathering processes (Dunlop and Özdemir, 1997; France and Oldfield, 2000; Kruiver et al., 2001; Maher et al., 2004).

6.2. Magnetostratigraphy

Initial NRM intensities (at room temperature) of the La Vedova samples are low (ranging between 0.002 and 0.05 mA/m). However, a sufficient number of samples (~80%) showed good quality thermal demagnetization diagrams, so that the direction of the characteristic remanent magnetization (ChRM) could be reliably interpreted. The remaining 20% had either extremely low NRM intensities, lost most of...
the NRM during low-temperature treatment and/or displayed random orientations (Fig. 4b, c and d). The ∼30° tilt (bedding orientation 116/30; strike/dip) helped to distinguish primary (pre-tilt) from secondary (post-tilt) components.

Generally, a randomly oriented viscous NRM component was removed during thermal demagnetization to 80 °C. Further heating revealed the removal of a second component between 80 °C and 180 °C, mostly of normal polarity. The directions of this component cluster around the present-day field directions and were interpreted as overprints. A third component progressively decays towards the origin and is in most cases completely removed at temperatures of 340/360 °C (Fig. 4b, c and d). This 180 °C–360 °C-temperature component has dual polarity and is interpreted as the primary ChRM component.

Plotting the ChRM directions on an equal area projection reveals a slight non-antipodality of the normal and reversed directions (Fig. 4e). This non-antipodality is explained by overlapping blocking temperature spectra of the primary and secondary greigite components, similar to that observed in the younger sediments at Monte dei Corvi (Hüsing et al., 2007, 2009). Although the mean directions do not pass the reversal test, we consider this component as a reliable recorder of the ancient palaeomagnetic field at time of deposition.

Plotting the ChRM in stratigraphic order clearly reveals three intervals of normal and three of reversed polarity (Fig. 5). Magnetic directions are less well defined in the lowermost part of the section due to lower NRM intensities and lesser quality of thermal demagnetization. As a consequence, the position of the lowermost reversal boundary is less well constrained. The long normal interval in the upper part of the section is much thicker than the other intervals, suggesting that it has a significantly longer duration.

7. Radioisotopic dating

Several volcanic layers have been identified in the La Vedova section (Fig. 5). Mader et al. (2001) dated the “Aldo level”, a volcanoclastic
long-term trends, and of changes in sedimentation rate (see Fig. 5).

distinct steps in the proxy records, of reversals and/or changes in intervals I, II, and III, to minimize the potentially disturbing effects of because of the distinct cyclic variability throughout the section.

not contain such large biotite size fractions of 160 up to 500 µm. Our A1 ash, however, certainly does correlate either with the A0 or the A2 ash layer. Here, we present new 40Ar/39Ar data on biotites of these two layers. We also tried to analyze K-feldspar fractions, but did not obtain reliable results. Standard mineral separation procedures have been used (for more details the reader is referred to e.g. Kuiper et al. (2008)).

Biotite of A0 yields an age of 14.87 ± 0.01 Ma (MWSD 1.14, n = 7/9) and biotite of A2 yields 14.76 ± 0.01 Ma (MWSD 1.01, n = 7/8) (Fig. 5; see also supplementary Table 2). Hence, we conclude that the Aldo ash most likely corresponds to A0. The ages increase to respectively 14.97 Ma and 14.86 Ma, if the recent astronomically calibrated age of 28.20 Ma for the Fish Canyon sanidine dating standard is used (Kuiper et al., 2008).

8. Initial age model and spectral analysis

The regular meter-scale variations in all geochemical proxies and magnetic susceptibility suggest a common origin, and we assume that they are linked to orbital forcing. This hypothesis can be tested by means of spectral analysis in the depth domain and, using an initial age model, in the time domain. Unfortunately biotite is not considered an ideal geochronometer, because of potential recoil and excess argon issues yielding older ages (e.g. McDougall and Harrison, 1999). Therefore, it is unwarranted to solely use these 40Ar/39Ar ages to check for cyclicity and pinpoint the astronomical tuning. We therefore build our initial age model on the magnetostratigraphic correlation to the ATNTS2004 (Lourens et al., 2004) in combination with the calcareous plankton biostratigraphy and 40Ar/39Ar ages of the ash layers.

8.1. Initial age model

The characteristic polarity pattern can be correlated straightforwardly to the interval between ~15.2 and ~14 Ma in the GPTS based on the constraints provided by the calcareous plankton bio-events, and the 40Ar/39Ar ages of Mader et al. (2001) and this study. The long normal polarity interval is correlated to Chron C5Adn and the lower two normal polarity zones to Chrons C5Bn.1n and C5Bn.2n, respectively, which is consistent with the pattern of our magnetostratigraphy. Consequently, we constructed an initial age model for the La Vedova section (Fig. 5) using the respective ages for the magnetic reversal boundaries in the ATNTS2004 (Lourens et al., 2004). The resulting age model reveals two sudden changes in sedimentation rate, the first at ~10 m and the second at ~20 m. The relatively high sedimentation rate of ~5.7 cm/kyr in the lower part of the section suddenly decreases to ~2.2 cm/kyr. In the upper part of the section the sedimentation rate increases again to ~4.9 cm/kyr.

8.2. Spectral analysis

Power spectra were calculated for the magnetic susceptibility and Ca/Al records in the depth and time domain, using the REDFIT-software of Schulz and Mudelsee (2002). These records were selected because of the distinct cyclic variability throughout the section. Spectra were generated for the entire section, but also separately for intervals I, II, and III, to minimize the potentially disturbing effects of distinct steps in the proxy records, of reversals and/or changes in long-term trends, and of changes in sedimentation rate (see Fig. 5). The magnetic susceptibility and Ca/Al records were transformed into time series using linear interpolation between and extrapolation beyond the six magnetostratigraphic calibration points for the interval between 15.29 and 14.17 Ma. Spectral analysis in the depth and time domain run over the entire section reveals distinct, relatively low frequency peaks (Fig. 6), which correspond to a cycle thickness of 2.79 m and a period of 113.89 kyr in magnetic susceptibility and of 2.84 m and 116.54 kyr in Ca/Al. In general, several peaks are present in the high-frequency part of the spectrum, corresponding to cycle thicknesses of 0.63, 0.77, 0.84, and 1.22 m and periods of, ~23, ~25, and ~35 kyr. Discrete spectra for the individual intervals reveal that intervals I and II have similar significant double peaks in the high-frequency band, corresponding to cycle thicknesses of ~0.75 m (0.64–0.87 m and 0.68–0.82 m). The dominant high-frequency period of ~13 and ~17 kyr in interval I changes to ~19, ~25 or ~34 (but not significant at 95% chi-squared level) kyr in interval II and is marked by a distinctly double (0.64–0.80 m) peak in interval II. Interval III reveals significant peaks equivalent to 0.62/0.61 and 1.20 m cycles, and periods of ~13 and 24.64 and 25.10 kyr, respectively. This indicates, that due to the significant increase in sedimentation rate in the upper part of our section (Fig. 5), the 1.20 m cycle component in interval III has the same period of ~25 kyr as the ~0.75 m cycle in intervals I and II. Evidently, although they range from 15 to 25 kyr, the periods of the most significant peaks cluster around 20 to 25 kyr indicating a dominant precessional origin.

Applying a ~0.75 and ~1.20 m bandpass filter in the depth domain reveals three intervals with high(er) amplitude changes in the filtered magnetic susceptibility and Ca/Al records around 5, 16 and 30 m (Fig. 7). These intervals correspond to ages of ~15.2, ~14.8, and ~14.4 Ma. The large-scale bundles in amplitude changes thus likely reflect the ~400-kyr eccentricity cycle, even though the number of extracted cycles does not perfectly match the interpretation (~20 precession cycles in a ~400-kyr eccentricity cycle) (this shortage of precession-related cycles is explained later on by the much lower sedimentation rates at times of ~400-kyr eccentricity minima when precession amplitudes are reduced). Low amplitude variations, which are particularly evident in the intervals marked by the thinly-bedded limestones at 10 and 21 m, correlate remarkably well with two successive ~400-kyr eccentricity minima at 15.0 and 14.6 Ma (see Fig. 8). Unfortunately, spectral peaks in the low frequency band of the spectra are not significant, which may be partly related to the short (~1 Myr) time series.

Amplitude variations also appear as bundles on a smaller-scale, encompassing 5 to 6 cycles of inferred precession origin (Fig. 7). Such patterns suggest the additional influence of the 100-kyr eccentricity cycle and are particularly well-expressed at 14.8 and ~14.4 Ma. The large-scale bundles in amplitude changes thus likely reflect the ~400-kyr eccentricity cycle, even though the number of extracted cycles does not perfectly match the interpretation (~20 precession cycles in a ~400-kyr eccentricity cycle) (this shortage of precession-related cycles is explained later on by the much lower sedimentation rates at times of ~400-kyr eccentricity minima when precession amplitudes are reduced). Low amplitude variations, which are particularly evident in the intervals marked by the thinly-bedded limestones at 10 and 21 m, correlate remarkably well with two successive ~400-kyr eccentricity minima at 15.0 and 14.6 Ma (see Fig. 8). Unfortunately, spectral peaks in the low frequency band of the spectra are not significant, which may be partly related to the short (~1 Myr) time series.

The potential influence of obliquity is not clear from the spectra. However, the occurrence of basic cycles showing alternating strong and weak peaks in magnetic susceptibility and the geochemical records (such as in Ti/Al, V/Al, Ca/Al and Zr/Al in the interval III) can be explained by precession–obliquity interference (see Fig. 2). This superimposed cyclicity would support the precession interpretation of the basic cycles.

8.3. Description and codification of cycles

Basic small-scale cycles could not be unambiguously identified on the basis of the lithological log alone. We therefore decided to number the successive filtered ~0.75 and ~1.20 m cycles in the magnetic susceptibility and Ca/Al and, combined with lithological information, we labeled these LV (La Vedova) cycles in Fig. 7. Numerals follow the filtered cycles and a, b, and c denote further subdivisions based on additional alternations of marls and limestones. Both intervals Ia and Ic can be further subdivided into an interval dominated by whitish thinly-bedded limestones (IaA and IcC), with lowest amplitude variations in the Ca/Al record, and an interval characterized by bluish thinly-bedded limestones (IaB and IcB; Fig. 7). In interval I, the basic
Fig. 7. Lithological column of the La Vedova section with cycle numbers (LV) according to the successive filtered $\sim 0.75$ and $\sim 1.20$ m-cycles in the magnetic susceptibility and Ca/Al combined with lithological information (see text for discussion). The magnetic susceptibility and Ca/Al records are shown with their filtered components in the depth domain (calculated using the Analyseries program of Paillard et al. (1996)). Band-widths of the filtered records are according to the power spectrum (Fig. 6). Note that intervals IIa and IIc are subdivided into an interval of thinly-bedded whitish limestones (IIa$_1$ and IIc$_2$) with low amplitude variations in Ca/Al and an interval of thinly-bedded bluish limestones (IIa$_2$ and IIc$_1$).
Fig. 8. Astronomical tuning of the La Vedova section to La2004(1,0.9) (Laskar et al., 2004) including information from magnetic susceptibility, Ca/Al record and the sedimentary cycle pattern.
precession cycle (~75 cm thick; Fig. 7) consists of a couplet of a thick grey or brown marl and an indurated thin whitish limestone. The basic cycle in interval II (64 to 80 cm thick) consists of a couplet of grey–greenish marl and white–bluish indurated limestone. Two (sub-)intervals (9.5–13.5 m and 18–22 m) are dominated by relatively thinly-bedded limestones, where the basic cycles (e.g. cycles 14, 16, 17, 19 and 20) often contain an additional thinly-bedded indurated limestone bed. In interval III, the basic precession-related cycle is about 1.2 m thick and consists of a couplet of a grey or green marl and a thick white or bluish more indurated limestone. Thinly-bedded whitish limestones are occasionally intercalated in the marl.

9. Astronomical tuning

9.1. Phase relation

Basic precession-related cycles in the Mediterranean Neogene consist of limestone–marl alternations (either with a couplet or quadruplet structure), sapropel–marl alternations, or marl–sapropel–diatomite alternations (triplets). The phase relation between limestone–marl couplets and precession is not constant and limestone beds can correspond to precession maxima/boreal summer insolation minima (e.g. Calabria; Hilgen, 1991) or to precession minima/boreal summer insolation maxima as in Monte dei Corvi (Hilgen et al., 2003). By contrast, the phase relation between sapropels and precession minima/insolation maxima remained constant (e.g. Hilgen et al., 1995; Hüsing et al., 2007) and the Monte dei Corvi limestones – in which sapropels tend to develop – were thus correlated to precession minima/insolation maxima (Hilgen et al., 2003). At La Vedova, bulk carbonate δ13C values (analogous for marl and limestones) explain why the bandpass filter in the depth domain and, starting from the initial magnetobiostratigraphic age model, in the time domain were unable to extract the expected larger number of precession-related basic small-scale cycles in magnetic susceptibility and Ca/Al in these particular intervals.

The tuning of the stratigraphic intervals below and above requires that all the thin limestone beds in intervals Ic2 and Ia1 correspond to single precession cycles, implying a significant reduction in sedimentation rates during ~400-kyr eccentricity minima (Lourens et al., 2001). This implies why the bandpass filters in the depth domain and, starting from the initial magnetobiostratigraphic age model, in the time domain were unable to extract the expected larger number of precession-related basic small-scale cycles in magnetic susceptibility and Ca/Al in these particular intervals.

9.2. Astronomical tuning of La Vedova

We selected the La2004(1,0.9) astronomical solution with present-day value for dynamical ellipticity and 0.9 for tidal dissipation for the tuning of the La Vedova section because it revealed the best fit with the detailed cycle patterns, especially those related to precession–obliquity interference, as we will demonstrate later on. This interference pattern as observed in the insolation time series depends on the values adopted for these two Earth parameters in the astronomical solution (Pälike and Shackleton, 2000; Lourens et al., 2001; Hüsing et al., 2007). As a first step in the tuning, the magnetostatigraphic calibration to ATNTS2004 (Lourens et al., 2004) provided six initial tie points between the sedimentary proxy cycles and the astronomical target curve (Fig. 8). Next, the first-order tuning to ~400-kyr eccentricity is constrained by the two intervals (Ila and Ilc) with thinly-bedded limestones and low amplitude variations in the proxy records that correlate with the two successive ~400-kyr eccentricity minima around 15.0 and 14.6 Ma. In between, the three intervals marked by prominent maxima in magnetic susceptibility, minima in Ca/Al (at ~12, ~14 and ~17 m), and distinctly greenish coloured marls in cycles 23, 24 and 25 and 29, correspond to the three successive ~100-kyr eccentricity maxima around 14.92, 14.82 and 14.72 Ma. Together, they constitute the ~400-kyr eccentricity maximum around 14.8 Ma, in which the two most distinct susceptibility maxima correspond to the most prominent insolation peaks. The 12 successive insolation minima that together constitute this ~400-kyr maximum can easily be recognized in Zr/Al and to a somewhat lesser extent in the Ti/Al record (see Fig. 2). The drastic change from thinly-bedded limestone beds in interval II to prominently thick and well-developed marls beds at 22.5 m (cycle LV 40) corresponds to the marked amplitude increase in insolation and precession following the ~400-kyr eccentricity minimum around 14.6 Ma (Fig. 8). The greenish marl of cycle LV 40 is thus well-correlated with the first pronounced insolation maximum at ~14.47 Ma. The regular alternation on the 2–2.5 m scale of thick indurated and thinner less-indurated limestone beds in interval III and the marked amplitude variations in magnetic susceptibility and Ca/Al (which is also present in the Ti/Al and Zr/Al records, see Fig. 2) fit remarkably well with the precession–obliquity interference pattern in the interval between 14.5 and 14.1 Ma in the insolation curve (Fig. 8). All basic cycles can be unambiguously correlated to precession and insolation. Note that slightly different alternative tuning options have initially been considered but that they lacked internal consistency and resulted in less constant spreading rates (see below and Hüsing (2008); Chapter 5).

The tuning of the stratigraphic intervals below and above requires that all the thin limestone beds in intervals Ic2 and Ia1 correspond to single precession cycles, implying a significant reduction in sedimentation rates during ~400-kyr eccentricity minima (Lourens et al., 2001). This implies why the bandpass filters in the depth domain and, starting from the initial magnetobiostratigraphic age model, in the time domain were unable to extract the expected larger number of precession-related basic small-scale cycles in magnetic susceptibility and Ca/Al in these particular intervals.

The good fit with most details in the insolation target curve, and in particular those related to precession–obliquity interference, indicates that 1) the inferred phase relation with precession is most likely correct and 2) the La2004(1,0.9) solution is a suitable solution for tuning this interval. Remarkably, the pattern in the insolation curve of the La2004(1,0.9) is almost the exact mirror image of the La2004(1,1.2) curve used as an alternative for the tuning of the interval older than 10–11 Ma at Monte dei Corvi (Hüsing et al., 2007). This implies that our cyclic patterns would reveal an excellent fit with the La2004(1,1.2) solution if we start from an opposite phase relation with precession. Note that we initially started from this opposite phase relation and used the La2004(1,1.2) solution for the tuning of La Vedova (Hüsing, 2008), but that we decided to alter the phase relation and, thus, solution because of the stable isotope (δ18O) evidence in combination with the ongoing study of the upward extension of the La Vedova section in the high cliffs.

Based on the astronomical tuning, we assigned astronomical ages to the midpoints of limestones in each basic cycle (see supplementary Table 3). Consequently, astronomical ages for biostratigraphic events and magnetic reversal boundaries were calculated by means of linear interpolation between the two nearest calibration points assuming constant sedimentation rates (Table 1). The La Vedova ages differ between 55 and 7 kyr from ages in the ATNTS2004. Part of the discrepancy can be related to small uncertainties in the ATNTS2004
reversal ages, since reversal ages older than CSAn (13.015–13.183 Ma) are based on interpolated ages derived from a seafloor-spreading-rate history model and lack astronomical calibration. Unfortunately, some uncertainties remain in the tuning of interval I. Matching sedimentary cycle patterns and variations in magnetic susceptibility and Ca/Al to insolation did not result in an excellent fit and thus provided a rather uncertain astronomical age for CSBn.2n(o). This uncertainty is reinforced by the poor quality of the paleomagnetic signal in this interval.

9.3. Testing and confirming the astronomical reversal ages using seafloor spreading rates

Evaluation of the most reliable magnetic reversal ages is possible through analysis of their implication for seafloor spreading rates (Fig. 9). We assumed that simultaneous apparent rate changes of the same ratio on multiple plate pairs are an artifact that results from time scale errors. The analysis included the astronomical reversal ages of La Vedova in the interval between 14.0 and 15.2 Ma (see Table 1), and ages of 13.691 Ma for CSAC(y) (Abels unpublished data), 13.55 Ma for CSAn(o) (Wilson unpublished data) and 15.974 Ma for CSCh(y) (Shackleton et al., 2001).

Our new reversal ages result in constant spreading rates and rate changes along all plate pairs, except for CSBn.2n, thus supporting our preferred tuning (see also Hüsing (2008); Chapter 5). The astronomical age of CSBn.2n(y) is too young and of CSBn.2n(o) is too old, which results in a too long duration for CSBn.2n. This discrepancy seems too large to result from any simple tuning problem. It is therefore likely that the paleomagnetic signal in this interval is distorted due to enhanced sulfidization processes involving iron oxide dissolution and iron sulphide formations in this interval, as suggested by the increased sulphur content between 10 and 11 m.

Furthermore, we can test our astronomical tuning by running spectral analysis on tuned time series. Spectral peaks should then be clear and correspond to the periods of orbital precession, obliquity and eccentricity. In addition, the noise in the data should be significantly reduced. The results show that precession and obliquity frequencies are much better resolved using the astronomical age model instead of the ATNTS2004 reversal ages (Fig. 6). In particular the period of the high-frequency spectra peak in interval 1 shifts from ∼15 to ∼20 kyr, which is in much better agreement with the main period of precession. However, it should be realized that this improvement is a consequence of the tuning itself and does not provide independent confirmation of astronomical control and/or tuning. Nevertheless, for interval III, spectral peaks of obliquity (42.4 kyr) in the Ti/Al and Zr/Al spectra independently confirm precessional forcing (22.6 kyr) (see supplementary data).

We suggest that our new astronomical reversal ages should replace ages in the ATNTS2004 for the interval in which the tuning is robust (14.2 to 14.9 Ma).

9.4. Comparison to alternative tunings and other records

An alternative tuning has been previously proposed for the interval between 8 and 22 m of the La Vedova section (Mader et al., 2004). Our tuning is consistent with their tuning at the ∼400-kyr scale, more specifically to the ∼400-kyr eccentricity maximum around 14.8 Ma. However, on the ∼100-kyr scale, we tune our two most prominent carbonate minima and corresponding magnetic susceptibility maxima to the two marked ∼100-kyr eccentricity maxima at ∼14.72 and ∼14.82 Ma. We demonstrate a precession origin for the dominant high-frequency cycle but, although precession/obliquity interference patterns are present, the dominance of obliquity as suggested by Mader et al. (2004) is not confirmed by our data (for a detailed discussion see Hüsing (2008); Chapter 5).

A dominant obliquity control in the interval between ∼15.1 and ∼14.7 Ma is also not supported by the high-resolution stable isotope records from the Pacific (Holbourn et al., 2007). However, a direct comparison to the stable records from ODP Sites 1146 and 1237 (NW and SW Pacific; Holbourn et al., 2007) is difficult because the Pacific sites lack a magnetostratigraphy, whereas a detailed isotope record is not available for our section. A strong ∼100-kyr eccentricity control in the interval between ∼15.3 and ∼14.55 Ma is observed in the Pacific isotope records and at La Vedova. The dominance of the ∼41-kyr obliquity cycle in the interval between 14.7 and 14.1 Ma in the Pacific is not recorded at La Vedova but the additional influence of obliquity is found superimposed on the precession dominance in some geochemical proxy ratios, such as Ti/Al and Zr/Al, which reveal precession–obliquity interference patterns in the interval between ∼14.5 and 14.2 Ma. This observation is consistent with the pattern in the insolation curve. However it should be realized that orbital controlled sedimentary cycles in the Mediterranean Neogene likely reflect regional rather than global climate change, and always show this influence of obliquity in addition to that of precession and eccentricity.

10. Environmental changes

10.1. Environmental and climatic significances of the basic precession-related cycle

The cyclic co-occurrence of maxima in redox-sensitive elements, such as Ba, V, and S, points to periodically increased primary

Table 1

<table>
<thead>
<tr>
<th>Stratigraphic position</th>
<th>Astronomical age (Ma)</th>
<th>ATNTS2004 age (Ma)</th>
<th>Δ (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSADn(y)</td>
<td>39.210 ± 0.110</td>
<td>14.153 ± 0.002</td>
<td>14.194</td>
</tr>
<tr>
<td>CSADn(o)</td>
<td>20.375 ± 0.055</td>
<td>14.609 ± 0.004</td>
<td>14.581</td>
</tr>
<tr>
<td>CSBn.1n(y)</td>
<td>15.775 ± 0.145</td>
<td>14.775 ± 0.005</td>
<td>14.784</td>
</tr>
<tr>
<td>CSBn.1n(o)</td>
<td>13.230 ± 0.060</td>
<td>14.870 ± 0.003</td>
<td>14.877</td>
</tr>
<tr>
<td>CSBn.2n(y)</td>
<td>10.615 ± 0.245</td>
<td>15.000 ± 0.010</td>
<td>15.032</td>
</tr>
<tr>
<td>CSBn.2n(o)</td>
<td>3.350 ± 0.860</td>
<td>15.215 ± 0.022</td>
<td>15.160</td>
</tr>
</tbody>
</table>

Biostratigraphic events

| influx Beginning G. debiscens | 8.060 ± 0.480 | 15.098 ± 0.011 |
| influx End of G. debiscens    | 12.210 ± 0.050 | 14.915 ± 0.003 |
| Acme b base Beginning of P. siakensis | 13.230 ± 0.060 | 14.870 ± 0.003 |
| second increase P. siakensis  | 14.175 ± 0.045 | 14.648 ± 0.187 |
| LCO H. waltrans              | 25.745 ± 0.205 | 14.414 ± 0.004 |
| top Acme b End P. siakensis   | 35.230 ± 0.050 | 14.234 ± 0.005 |
productivity and/or suboxic to anoxic conditions on a precessional time scale (Goldberg and Arhenius, 1958; Schmitz, 1987; Lea and Boyle, 1990; Dymond et al., 1992; Francois et al., 1995; Wehausen and Brumsack, 1999), similar to those inferred for sapropel formation in the younger Monte dei Corvi and other Neogene sections in the Mediterranean (e.g. Rossignol-Strick, 1985; Rohling and Hilgen, 1991; Rossignol-Strick, 1993). Even though sapropels are not noticeably developed in the La Vedova section, the basic small-scale cycle is dominantly precession and eccentricity controlled, even at times that δ18O records from the Pacific reflect a dominant obliquity control on most likely glacial cyclicity (Holbourn et al., 2007). The fact that typical sapropels are not developed during the Langhian may indicate that the basin was not yet sensitive (enough) for the formation of sapropels. A more thorough account on the elemental signature of the cycles will be presented in a separate paper dealing with the geochemical elemental records of the entire La Vedova composite section.

Fig. 9. Reduced distance tests for constant spreading rates along six plate pair astronomical ages resulting from the astronomical tuning. Observed spreading distance (D) is plotted against age (in Ma), after subtracting predicted distance according to a constant spreading rate (R). Errors in the time scale will plot as uniform vertical departures from the reduction line R (see text for discussion).
10.2. Other controls on environmental changes

The geochemical proxy record of La Vedova also shows non-repetitive changes unrelated to astronomical climate forcing, which can now be astronomically dated. In interval I, between ~15.3 and 15.074 Ma, elevated Ba, S and V contents suggest increased productivity and/or increased preservation of organic matter, which is explained by increased river input during warm and wet climates (Wehausen and Brumsack, 1999, 2000) or by changes in sediment fluxes. The resulting suboxic bottom water conditions (increased V, a redox-sensitive element) led to an intensification of sulphidization processes as indicated by increased sulphur contents. The first discrete step marked by a sudden drop in Ba, V, and S and the increase in Zr at 15.074 Ma (cycle 12) might be linked to reduced riverine discharge and hence climatic cooling (Wehausen and Brumsack, 1999, 2000) and might signify an environmental and climatic change preceding the Middle Miocene climate shift at 13.82 Ma (Abels et al., 2005; Holbourn et al., 2005). The abrupt change coincides closely with the end of the Middle Miocene Climatic optimum between ~17 and ~15 Ma (Zachos et al., 2001). Evidently, the 400-kyr eccentricity cycle played an important role in this change as it markedly coincides with the beginning of the ~400-kyr eccentricity minimum at 15.06 Ma. However, the ~400-kyr eccentricity cycle is not solely responsible for this shift because similarly enhanced Ba, V and S values do not return higher in the section following the eccentricity minimum. The uninterrupted reduced Ba content in interval II indicates colder climatic conditions relative to the time interval before ~15.074 Ma.

The second discrete step marked by a sudden increase in magnetic susceptibility and drop in CaCO3 and Ba occurs at 14.489 Ma and is associated with a major increase in thickness of the basic cycle from ~0.75 m in intervals I and II to ~1.20 m in interval III and, hence, an increase in sedimentation rate (Figs. 2 and 5). The remarkable synchrony of these changes can either be related to changes in local tectonic processes or changes in regional or global climate, which can both result in enhanced detrital input. Evidently, also this step is at least partly related to the ~400-kyr eccentricity cycle as it coincides precisely with the end of the ~400-kyr eccentricity minimum around 14.6 Ma. The decrease in CaCO3, Ba, and S, and more pronounced peaks in Ti and Zr, may indicate a further step in aridification of the climate. The latter might be related to the climatic deterioration between 15 and 14.5 Ma (Vincent and Berger, 1985; Woodruff and Savin, 1989: Flower and Kennett, 1993, 1994; Zachos et al., 2001; Shevenell and Kennett, 2004; Shevenell et al., 2004). The second environmental step at La Vedova slightly postdates – and is therefore not directly linked to – the switch from ~100-kyr eccentricity to ~41-kyr obliquity dominance around 14.7 Ma observed in Pacific δ18O isotope records (Holbourn et al., 2007).

The influence of the ~400-kyr eccentricity cycle may have occurred superimposed on long-term climatic or directional tectonic trend(s), exerting an additional control in passing certain thresholds at discrete steps in time during the middle Miocene. Such distinct steps may thus specifically result from – or be amplified by – the combination of a long-term climate or tectonic trend and the ~400-kyr eccentricity cycle. The influence of the ~400-kyr eccentricity cycle is also found in the marine record from Malta in the interval between ~13.9 and ~12.7 Ma (Abels et al., 2005) and at Monte dei Corvi (Hüsing et al., 2009a). Superimposed on the long-term Middle Miocene cooling trend, this long-term cycle may have played an important role in pushing the global climate stepwise into a cooler mode culminating in the Middle Miocene Climatic transition, which also occurred during the ~400-kyr eccentricity minimum around 13.8 Ma. As long as there are no reliable ages available for the tectonic constriction and final closure of the eastern Tethys seaway (Hüsing et al., 2009b), the marine connection between the Mediterranean and Indian Ocean, it remains problematic to separate the impacts resulting from this directional trend from the long-term climatic cooling in the Middle Miocene.

11. Conclusions

Spectral analysis of high-resolution magnetic susceptibility and geochemical proxy records in the depth and time domain demonstrate that the various scales of cyclicity observed in the sediments of the magnetobiotestratigraphically well constrained La Vedova are related to the astronomical cycles of precession, obliquity and eccentricity and thus to astronomical induced oscillations in climate. Precession and eccentricity (through modulating the precession amplitude) are dominant with obliquity playing a secondary but important role. The inferred phase relation with maxima in Ca/Al, redox-sensitive elements and Ba, and minima in magnetic susceptibility corresponding to precession maxima, and obliquity and boreal summer insolation minima is opposite to the phase relation found at Monte dei Corvi.

Starting from a first-order calibration to eccentricity, the basic precession-related cyclicity could be tuned to the precession and insolation time series of the La2004.1(e) solution. The good to excellent fit with characteristic details that result from precession-obliquity interference indicates that this is the preferred solution for this time interval. The tuning is corroborated by analysis of seafloor spreading rates of six plate pairs assuming constant or constantly changing spreading rates. Because of the robust tuning, our ages between 15.29 and 14.17 Ma except for CSAnb.2n(o) should replace existing ages in the ATNTS2004 calculated from spreading distances and lacking direct astronomical control.

Two major steps in the geochemical proxy records, dated astronomically at 15.074 and 14.489 Ma, coincide with abrupt changes in sedimentation rate. They resulted from the combined effect of the ~400-kyr eccentricity cycle superimposed upon a longer-term climatic or tectonic induced trend. Although sapropels are not developed at La Vedova, a dominantly precession controlled oscillatory climate system similar to that responsible for sapropel formation in the Neogene Mediterranean was operative from at least ~15.3 Ma onwards.

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Appendix A. Supplementary data


References

