Cychrochronology of the Massignano section Global Stratotype Section and Point for the E/O Boundary and the MassiCore (central Italy).

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Abstract…

1. Introduction

The Eocene Oligocene Transition (EOT) marks a momentous shift in the climate history of Earth when our planet transitioned from an ice-free, greenhouse, state to an ice-house state characterized by the presence of a large and persistent ice-sheet over Antarctica. This transition is primarily reflected in marine ∂18O records where a positive shift of ~1.5‰ occurs (Miller et al., Zachos et al, 2001; …etc…), as well as in Antarctic records (Kennedy-Asser, 2020 and Galeotti et al., 2021, with references therein). The emplacement of an Antarctic ice-sheet at the EOT was a relatively rapid event occurring in two main steps as captured by sufficiently well-resolved oxygen isotope records (Coxall et al., 2005 etc.). This major climatic transition was preceded by longer-term changes toward globally cooler conditions and periods of accelerated climatic deterioration. The Massignano section (Fig. 1 – location map) is a key locality for the reconstruction of the climate history accompanying the EOT because it has been defined as the Global Stratotype Section and Point (GSSP) for the Rupelian stage (Pomerol and Premoli Silva, 1988), corresponding to the Eocene/Oligocene Boundary. Unfortunately, analyses of the magnetostratigraphy of this reference succession (Bice and Montanari, 1988; Lanci et al., 1996; Jovane et al., 2007) provide largely different results (Fig. 2 litho-, bio- and magnetostrat-), which prevents a confident correlation of the upper Eocene of Massignano to global records of climate change. To extend the lower Oligocene record in the Massignano area, a xx m-thick succession, the so-called Massicore, was drilled ~100 m south of the Massignano GSSP section (Montanari et al., 1994; Lanci et al., 1996). The core includes an additional 15-meter record of lower Oligocene on top of the record exposed in the Massignano GSSP section. Here we obtain a fine-tuned composite record of the Massignano section and Massicore, based on splicing the magnetic susceptibility and CaCO3 record from the two sites. The obtained record spans the top magnetochron C16n to lower C12r. We provide a cyclochronological interpretation across the composite record, which is of relevant for high resolution correlation of the E/O GSSP worldwide.

2. Material and Methods

The Massignano section, located in the Umbria- Marche Basin (figure 1), is the currently accepted type section for the Eocene/Oligocene boundary (Premoli Silva and Jenkins, 1993). The 23 m-thick sedimentary succession outcropping in an abandoned quarry covers the latest Eocene to earliest Oligocene and consists of reddish and greenish-gray hemipelagic marls and calcareous marls

belonging to the Scaglia Variegata and Scaglia Cinerea formations (Figure 2). Several studies provide an integrated biostratigraphic framework of the section (Coccioni et al., 1986, 1988; Coccioni, 1988; Nocchi et al., 1988; Parisi and Coccioni 1988; Bellagamba and Coccioni, 1990; Brinkhuis and Biffi, 1993) (see Fig. 2). Likewise, different authors have analysed the magnetostratigraphy of the Massignano GSSP providing slightly different results, possibly in relation to the different stratigraphic resolution adopted (Bice and Montanari, 1988; Lowrie and Lanci, 1994; Jovane et al., 2007). The Massignano core (MassiCore) was drilled at about 110 m south of the Massignano stratotype section covering the entire stratigraphic and the very same stratigraphic sequence is expected. A high-resolution record of magnetic susceptibility is available (Lanci and Lowrie, 1997) allowing to to precisely correlate the MassiCore with the GSSP section. High resolution magnetic susceptibility and wt.% $CaCO_3$ records are available for the Massignano GSSP (Jovane et al., 2004). For the Massicore a lower resolution record (10 cm-spaced on average) is available from Lanci (1995; Phd Thesis. (Fig. 2).
After precise correlation both records have been analyzed using a suite of spectral analyses to detect periodicity that could potentially track the sedimentary expression of astronomical forcing. These include Wavelet and Multi Taper Method (MTM).

3. Previous cyclochronological studies of the Massignano GSSP

A high-resolution analysis of the variations in the composition, concentration and grain-size of magnetic minerals from the Massignano GSSP has been conducted by Jovane et al. (2004) who also provided wt. %CaCO3 from the same sample set yielding ~5 cm-spaced records of these parameters. Jovane et al. (2004) reported large variations of the magnetic properties through the Massignano GSSP. On this basis, they distinguished six zones of contrasting magnetic properties of high and low magnetic mineral concentrations (determined by the magnetic susceptibility, intensity of natural and artificial remanences and hysteresis parameters) that do not correspond to the main lithostratigraphic boundaries (Fig. 3). Considering the stratigraphic extent of magnetocrhons identified at Massignano by Lowrie and Lanci (1994) against the Geomagnetic Polarity Time Scale of Cande and Kent (1995), Jovane et al (2004) derive an average sedimentation rate of 0.69 cm/kyr, which suggests a total duration of ~400 kyr for the alternating intervals of low and high magnetic minerals concentration. On this basis Jovane et al. (2004) suggest a ”the existence of an external forcing mechanism (long-term eccentricity cycle) that drove sedimentary processes before the major cooling at 33.55 Ma (Oi-1 event)”. According to Jovane et al. (2004) the absence of these 400 kyr-long intervals in the upper part of the section, corresponding to Chron C13r, would indicate that a threshold level was passed in the climate system before the Oi-1 cooling event, which caused a nonlinear response of the sedimentary processes to astronomical forcing. We note that a duration of 400kyr of the alternating intervals characterized by different magnetic properties would entail a 800 Kyr period of the forcing mechanism, which is, therefore, not ascribable to long eccentricity.
Using the data set provided by Jovane et al. (2004), Jovane et al., (2006) conducted a spectral analysis of the magnetic susceptibility (χ) and wt. % CaCO3 records of the Massignano section. According to Jovane et al. (2006), spectral analyses of the (residuals) χ and wt. % CaCO3 records show peaks of spectral density at ~70 cm and ~32 cm, that can be confidently interpreted to reflect the short eccentricity and obliquity, respectively. The detection of a 1.2 Myr modulation of the obliquity component in the χ record was taken to provide a decisive constraint on the obtained orbital tuning. According to Jovane et al. (2007), obliquity dominates the record of the Massignano section providing a metronome for the orbital tuning of the E/O boundary GSSP. Periods of higher χ appear to be in phase with higher obliquity providing a phase-relationship

useful to derive a paleoceanographic interpretation of astronomically controlled sedimentary processes for the Massignano GSSP. The analysis conducted by Jovane et al. (2006) has been limited to the stratigraphic interval spanning meter 4 to 20 of the Massignano GSSP. Here we extend their analysis to the entire sedimentary succession exposed in the Massignano Quarry spanning 0-23 m.

4. Results

4.1. Cross-Correlation of the Massignano GSSP and the MAssiCore.

The MassiCore has been drilled in a close proximity to the Massignano Quarry to obtain a twin stratigraphic succession that extends the Oligocene portion available in the GSSP area (Montanari et al. ??). Indeed, the Massicore extends well above the E/O boundary to the lower part of Chron C12r whereas the Massignano section includes only a part of Chron 13n. Furthermore, the base of C13n is poorly defined in the Massignano GSSP section, which is not ideal to define a chronology of the EOT in the type section of the E/O boundary that can be exported to other sites. The available magnetostatigraphy and the cross correlation based on the MS records allows to confidently compare the cyclochronology obtained at the two sites.

We have achieved an optimal correlation of the Massignano GSSP section and the MassiCore by performing a cross correlation between the MS record of the two successions.
Before computing the cross-correlation function we have reverted the core depth assign the zero value to the core bottom and interpolated both records to the same depth sampling interval of 5 cm. Results show the largest correlation is found when the MASSICORE susceptibility record is lagged on 11 units (i.e., 55 cm) with respect to the Stratotype section (Fig. 3).

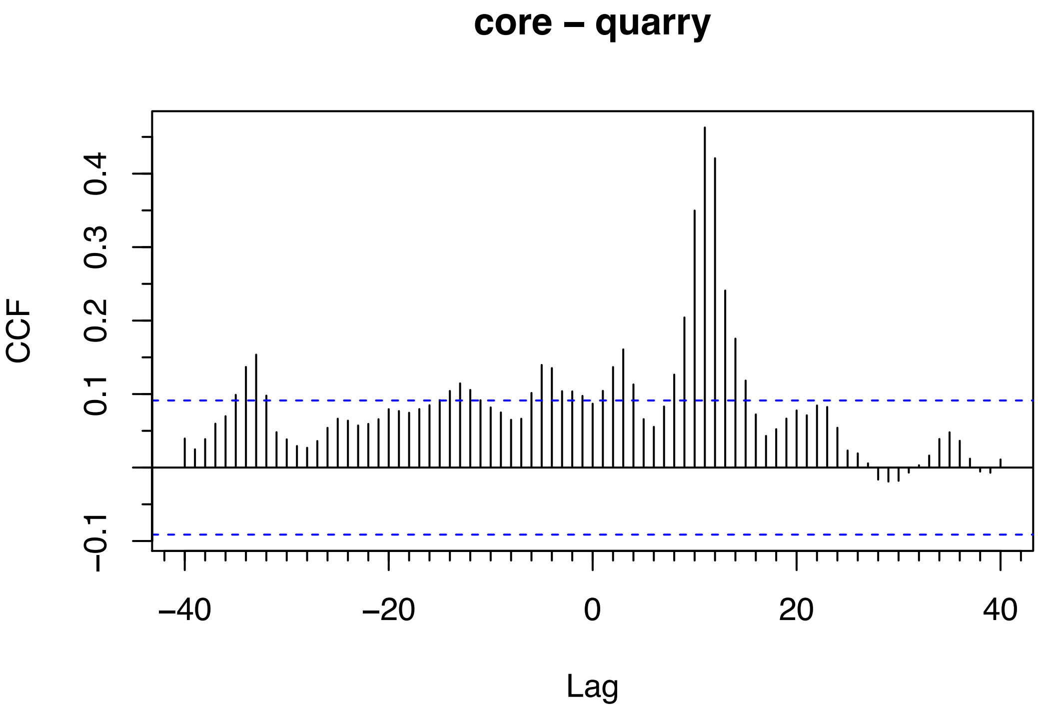


Figure 3. Scores of the cross-correlation between MS records of the Massignano GSSP and the Massicore. The highest score, after setting the base of the core to level 0 is found at 11 point (corresponding to 0.55 m)

A depth scale for MASSICORE that matches the depths of the stratotype section was then calculated. As expected (Lanci et al. 1996), the MASSICORE covers virtually all the stratotype section and extends the record at the top of it for about 10 m (Fig. 4).

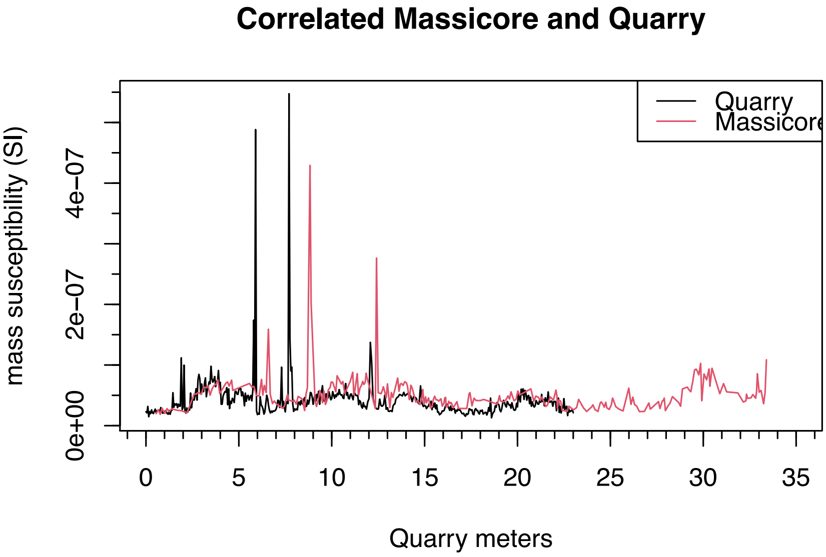


Figure 4 – Splice of the Massignano GSSP section and the MassiCore MS records.

However, there is a clear offset of 55 cm between the two records in the interval spanning the base of C15n to bottom core when compared to the Massignano Quarry record. This is particularly evident when correlating the major spikes of the MS record in the lower part of the two records (Fig. 4). Such a lag could derive from errors in the measure of the stratigraphic thickness in the field. However, we note that magnetochron C15n is shorter by ~60cm in the MassiCore (Lanci and Lowrie, 1997) compared to the Massignano GSSP section (Jovane et al., 2004), suggesting the occurrence of a small gap in the MassiCore that explains the observed difference. For this reason, and also considering the limited resolution of the MS record available, we limit the cyclochronological analysis of the MassiCore to the interval spanning C13r to the lower part of C12r.

For this stratigraphic interval an optimal correlation based on the MS records of the two sites allows to confidently project the C13n/C13r boundary, which is neatly defined in the MassiCore (Lanci and Lowrie?), to the Massignano GSSP where the magnetostratigraphic record is characterised by a loose definition of the base of Chron C13n. As a confirmation of the robustness of the cross-correlation, the E/O boundary, defined in the Massignano Quarry at meter 19 (Premoli and Jenkins, 1993) and meter 17.7 m in the Massicore (Van Mourik and Brinkhuis, 2005), shows a perfect coincidence between the two records. (Fig. corr.ai). On this basis the base of magnetochron C13n is projected in the Massignano Quarry at 21.05 m (Fig. corr.ai). This level is higher than the base of C13n proposed by Bice and Montanari (1988) but within the range of magnetostratigraphic uncertainty of Lowrie and Lanci (1994).

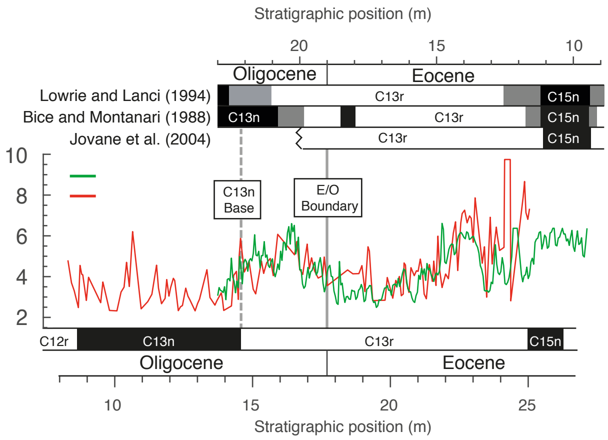


Figure corr.ai

4.2. Spectral analysis

In spite of the different sampling resolution adopted (~10cm in the Massicore and 5cm in the Massignano GSSP), wavelet transform analysis of the MS reveals the same evolutive spectral structure at the two sites. Minor differences, likely related to the different sampling resolution of the two records, do occur.

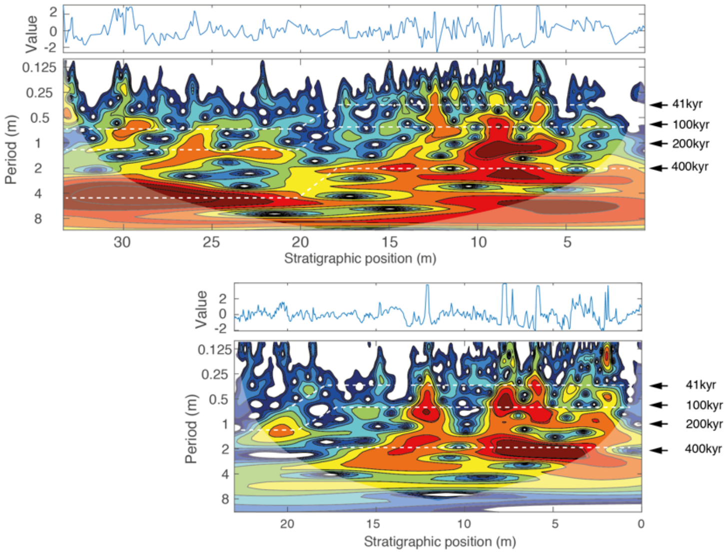


Figure 5. Wavelet transform of the MS record of the Massignano Quarry and the MassiCore.

Across C16n to the lower part of C13r, both records are characterized by relatively continuous crests of high spectral density at wavelengths of ~30 cm and ~70 cm, and ~2.5 m (Figure 5), periodicities that have been interpreted to represent the sedimentary expression of obliquity, short eccentricity and long eccentricity, respectively, by Jovane et al. (2006) based on the analysis of the 4-20 m interval in the Massignano GSSP section. Both records provide evidence for high spectral density at ~1.4 m wavelength, corresponding to ~200kyr. This could represent the 200 kyr beat recently described by Hilgen et al. (2020) from the the lower Paleocene of the Zumaia section. Both records show an obvious change in the spectral structure centered at ~17 m in the Massignano GSSP section and ~ 21 m in the MassiCore.

From 18m upward the more extended record of the Massicore is characterized by spectral densities confined to wavelengths of ~0.25, ~0.5 m, ~1.2 m and ~5m, which, considering the wavelength ratios, might represent precession, obliquity, short eccentricity and long eccentricity, respectively. The break observed in the wavelet spectra in a corresponding stratigraphic interval at the two site would, therefore, represent a large increase in sedimentation rate. Another, minor, change in sedimentation rate seems to occur in the lower part of the GSSP record with the lowermost 5 metres seem characterized by a slightly higher sedimentation rate compared to the interval between 5m–17m. Because of the occurrence of this breaks in sedimentation rate continuity, we filtered the short eccentricity component from distinct segments. In particular, the Massignano GSSP has been subdivided into three segments including 0-6(5.65) m, 5-17(16m) m and 16-23 m. MTM analysis the $CaCO_3$ and MS records from these distinct segments (see supplementary information) suggest to adopt a filter centered at 1.1 cycle/m between 0-6m; 1.4 cycle m between 5-17m and 0.85 cycle m between 16-23 m. On the same basis (see supplementary information) we adopt a filter centered at 1.4 cycle/m for the interval between 25 m (corresponding to the top of C15n) and 20.5 m. A filtered centered at 0.85 cycle/m has been used to filter the short eccentricity signal from 21.5 to the top of the core record. For each frequency a gaussian filter with a bandwidth corresponding extended to ±15% oif the filtered frequency has been adopted. Filtering of these components shows a remarkable record of modulation of the short eccentricity component by the 405 kyr period in C13r to C12r (Fig. 6), which provides a validation of the cyclochronological interpretation based on the wavelet spectrum. In particular, the filtered eccentricity signal from the Massicore provides evidence for the occurrence of 405 kyr maxima coinciding the C15n-C13r and slightly preceding the C13r/C13n magnetostratigraphic boundaries in line with observation from the other sites in the Pacific (Westerhold et al., 2014). It should be noticed that a correct identification of the 405 kyr maximum close to the C13r/C13n boundary is hampered, in the Massicore record, because of the occurrence of a ~40 cm interval with no samples, resulting in an apparent maximum at 14.5m. A correlation of the two sites base on MS records (Figure corr.ai I) allows to correctly place the 405 kyr at 15.7 m in the Massicore, that is to a short eccentricity cycle before the C13n/C13r magnetochron boundary. A further validation comes from the wavelet analysis of the $CaCO_3$ record after independently transferring it to the time domain using the age model obtained with the short eccentricity filter of the MS record (see Fig. S1).

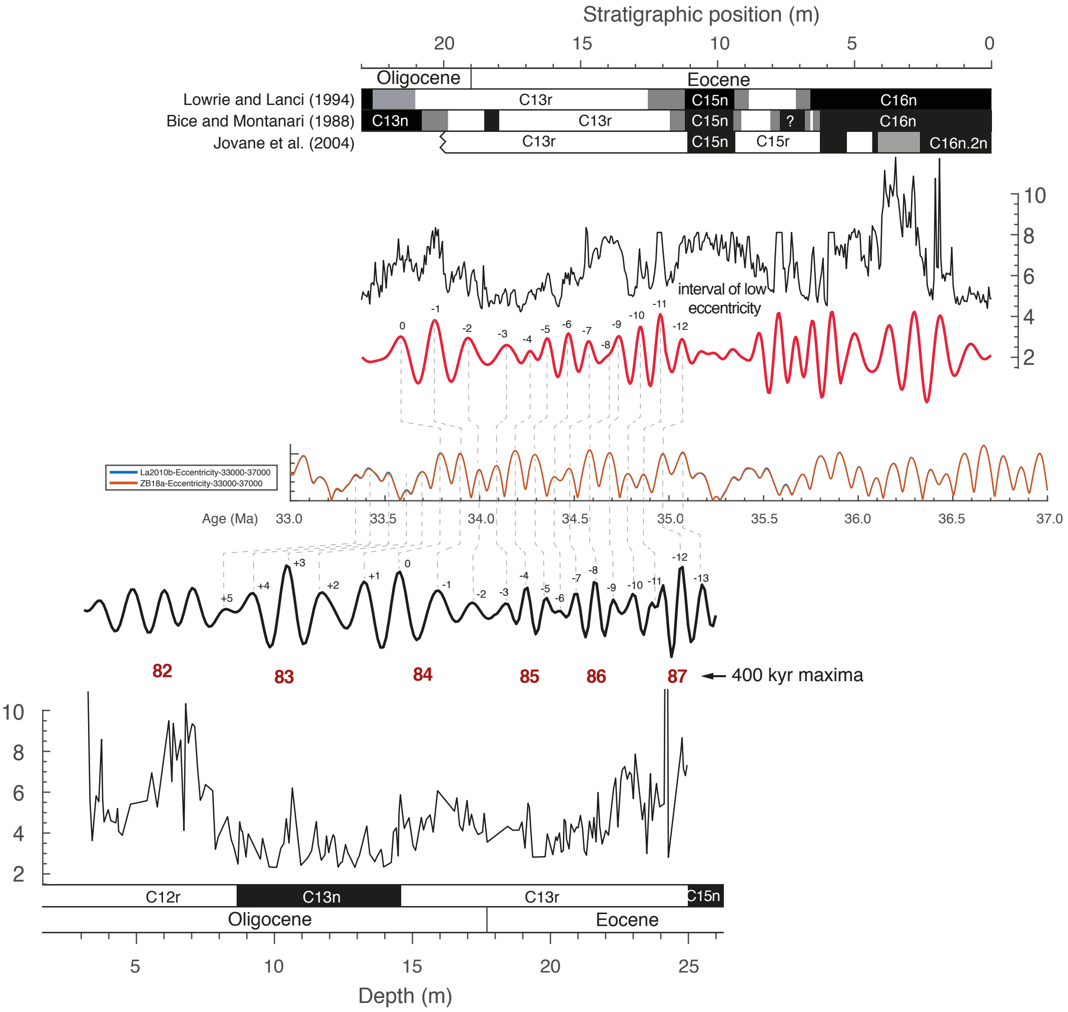
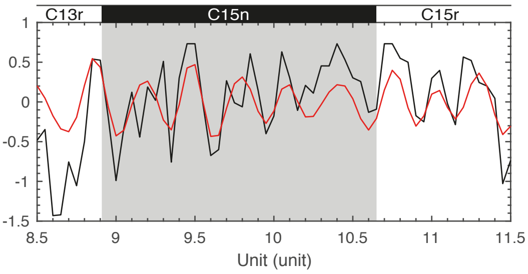


Figura Chronology.ai

In spite of the different sampling resolution the short eccentricity component filtered from the MS shows remarkable similarities in terms of cycle counting . In particular, at both sites, the short eccentricity filter shows a modulation by the long eccentricity term in the interval spanning C13r and in C13n, although not completely evident in the lower part of C13r in the Massignano GSSP record (Figura chronology.ai). The interval corresponding to magnetochron C16n.2 to the lowermost part of C13r is characterized by peaks of MS values corresponding to biotite-rich levels (Montanari et al ??), which is likely obliterating the long eccentricity modulation. For this reason, we do not expect a clear modulation of short eccentricity in this part of the stratigraphic successions studied. This interval is characterized by a lower sedimentation rate, in line with the observation of Jovane et al. (2006), which makes it difficult to correctly resolve the cyclochronology based on the ~20 cm sampling rate available for the MassiCore. Still, the composite of the two records allows to obtain a cyclochronological estimate of the duration of individual magnetochrons from C16n.1r to C13n. The latter is reported in table 1 together with the most recent estimate from the Geological Time Scale 2020 (GTS2020, Speijer et al., 2020). The C15n-C15r interval from the Massignano GSSP presents a weak signal in the band of short eccentricity (Fig. C15n-C15r interval MTM). Accordingly, the C15n-C15r interval corresponds to a 2.4 Myr node of low eccentricity modulation (Westerhold et al., 2014). For this reason, we carried out a cyclochronological estimate based on filtering the obliquity component across the 6-11.5 m stratigraphic interval, which allows to count 5.5 obliquity cycles within C15n and 8 obliquity cycles within C15r in the Massigno GSSP record (Figura obliquity C15n_C15r).



Because of the aforementioned potential problems in terms of continuity across magnetochron C15n the extent For the Massicore 25.5-17 m, 16-21.5 and 21-to top core in the MassiCore. Cycle counting in the Massicore allows to detect 12.5 short eccentricity within C13r and 4.5 short eccentricity cycles within C13n.

Magnetochron	Estimated duration MassiCore	Estimated duration Massignano GSSP	Jovane et al. (2006) Massignano GSSP	GTS 2020
C13n	~450 kyr			512±10 kyr
C13r	~1250 kyr			1376±41 kyr
C15n		~220 kyr	320 kyr	234±49 kyr
C15r		~320 kyr	383 kyr	245±31 kyr
C16n.1n		~150 kyr		138±36 kyr
C16n.1r		~150 kyr		56±42 kyr

Table 1. Summary of the cyclochronological duration of magnetochrons (C16n.1r to C13n) from the Massignano GSSP and the Massicore.

5. Discussion

5.1. Astrochronology of the E/O transition in the Massignano GSSP

The late Eocene and early Oligocene are well constrained in terms of astrochronological dating. The most recent astrochronological estimates for this time interval show only minor change compared to previously published Geomagnetic Polarity Times Scales (Speijer al., 2020). The maximum deviation regards the base of C12r, which has been recently dated at 33.214 Ma (Westerhold et al., 2014) compared to a previous estimate of 33.157 (GTS 2016). The base of Chron C13n is now dated to 33.726 Ma based on the analysis of multiple sites in the Equatorial Pacific (Pacific Equatorial Age Transect or PEAT) (Westerhold et al. 2016). The GSSP for the Eocene–Oligocene (E– O) boundary in Massignano is denoted by the extinction of the *Hantkeninidae* (Premoli Silva and Jenkins, 1993), which are, unfortunately, not preserved in the PEAT sites. As an alternative method for determining the astrochronological age of the E/O boundary, Westerhold et al. (2016) consider its occurence 14 % down in Chron C13r (Luterbacher et al., 2004), which provides an absolute age of 33.89 Ma for this chronohorizon. This estimate is ~ 100 kyr older than the age obtained by Pälike et al. (2006) but is in line with the astronomically tuned age from the Massignano GSSP proposed by Brown et al. (2009) based on cycle counting and absolute age constraints provided by three radioisotopic dating points (Montanari et al., 1988). Accordingly, considering the extinction of Hantkeniidae to be coeval with the δ18O plateau that follows the first positive step across the EOT oxygen isotope shift (Pearson et al., 2008) an age of 33.89 Ma for the E–O boundary is obtained in the PEAT sites.

Nevertheless, no astrochronological age estimate of the E/O boundary in the Massignano GSSP based on its proximity to the well dated base of C13n is available because of the loose definition of this chronohorizon in this section. The correlation of the Massignano GSSP with the nearby Massicore provides this opportunity. In order to provide a fine-tuned cyclochronology for the interval spanning the base of C13n to the E/O boundary, we carry out a spectral analysis of the MS and wt. % CaCO3 records between 17-23 m in the Massignano GSSP section. Considering an average sedimentation rate of ~1.2 cm/kyr (see above), the MTM analysis of both records shows high spectral density at the frequency expected for short eccentricity, obliquity and precession (Figure EOT chronology.ai). Filtering of the short eccentricity component evidences the occurrence of a number of cycles slightly exceeding 2.5, which provides total duration of ~250 kyr. Counting individual peaks in the wt.% CaCO3 and MS records reveals a number of 13.5 (in MS) to 14 (in Wt.% CaCO3) precessional cycles for a total duration between 283–294 kyr (Figure EOT_chronology.ai).

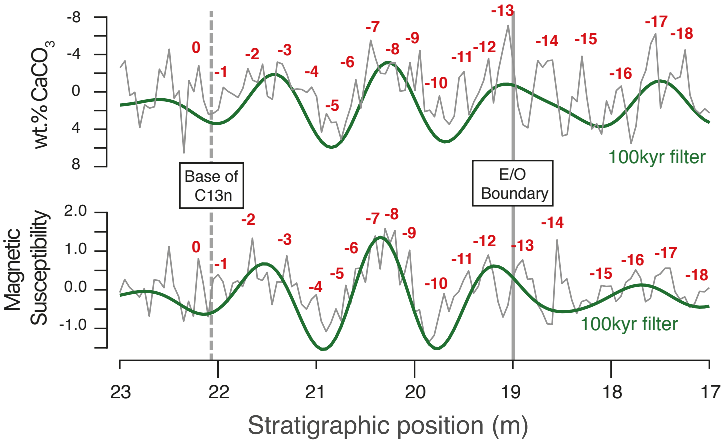


Figure EOT_chronology.ai. (Y axis revered for CaCO3).

Considering an astrochronological absolute age of 33.726 Ma for the C13n/C13r magnetochron boundary precessional cycle counting provides an age of 34.014 Ma for the E/O boundary in the Massignano GSSP, ~100 kyr older than reported by Westerhold et al. (2014) from the PEAT record and Brown et al. (2009) from the Massignano GSSP section itself. We note, however, that, assuming a C13n base to occur at 22.05 m as suggested by the correlation with the Massicore, the cyclochronology of Brown et al. (2009) provides a total duration of ~1.2 Myr for the C13r, which is shorter that the estimated duration provided here (1.25 Myr) and even more so than published in other records (see Speijer et al., 2020). More importantly, the top of magnetochron C15n (set at 11m according to Jovane et al., 2004) falls on an ascending flank of the 405 kyr modulation of eccentricity while the projected base of C13n (at 22.05 m based on the cross-correlation with the MassiCore record) coincides with a minimum in the astrochrological interpretation of Brown et al. (2006), which is at odd with the available astrochronology of this interval. In fact, the base of Chron C13n and the top of C15n rests on a descending flank and near the top of a 405 ky maximum in other records (Pälike et al., 2006; Westerhold et al., 2014), respectibely, in line with the well-expressed modulation of the short eccentricity component filtered from the MS Massicore record (Fig. Chronology.ai).

5.2. The Massignano cylochronological record in a global context

The most striking feature evidenced by the spectral analysis is the large increase in sedimentation rate occurring in both the Massignano GSSP section across the upper part of C13r as evidenced by the wavelet transform analysis.

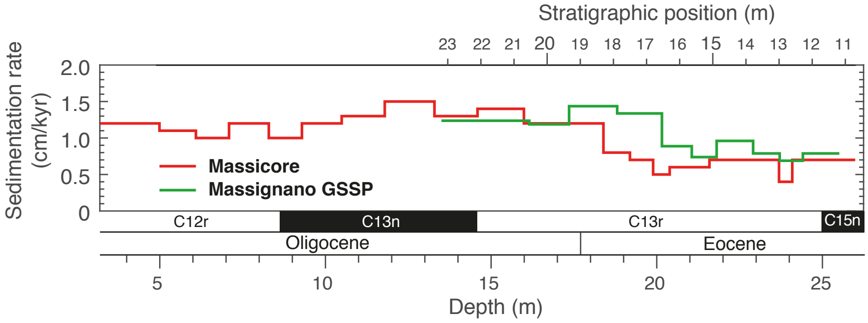


Figura sed rate

This transition to higher sedimentation rates can be better constrained by constructing an age model based on the filter of the short eccentricity component. In this age model each short eccentricity cycle is considered have a duration of 100 kyr. The resulting picture (Figura Sed Rate) shows a neat transition from an average value of ~0.7 cm/kyr to ~1.3 cm/kyr do occur with these same values in both the Massignano GSS and the Massicore records, although more gradual in the Massicore likely because differences in the filtering the two records. This observation is in line with geological records providing evidence for a prominent deepening of the calcite compensation depth (CCD) of more than 1km near the Eocene/Oligocene boundary (van Handel et al., 1975) in coincidence with the first appearance of a continental scale ice sheet on Antarctica (Kennett and Shackleton, 1076; Miller et al., 1991; Zachos et al., 1996; Coxall et al., 2005; Galeotti et al., 2016). Unfortunately, the oxygen isotope record of the Massignano GSSP is not well preserved, which does not allow a direct comparison with the associated ∂18O shift. Indeed, a trend to generally lower values is observed in the ∂18O across the EOT at Massignano, which is at odd with global values. The increase in sedimentation rate, however, is first captured at ~400kyr (~4 short eccentricity cycles) younger than the base of C13n, or ~100 kyr younger than the E/O boundary, which corresponds to an astrochronological absolute age of ~34.1 Ma, coinciding with the start of the ∂18O shift in astrochronologically dated and geochemically well-preserved oceanic records (Coxall et al., 2005 + altri). An independent confirmation that the Massignano GSSP succession captures the global increase in carbonate accumulation rate related to emplacement of the Antarctic ice sheet come from the ∂13C record, which is preserved in the local record and can, therefore be compared to other records globally. The emplacement of a continental scale ice-sheet at the EOT is also tracked by a prominent positive shift of ∂13C values (Coxal et al., 2005) tracking the impact of this event on carbon cycle feedbacks (Zachos and Kump, 2005). The ∂13C record of the Massignano GSSP shows an abrupt increase of ~0.6 ‰ starting at 17 m and culminating at 17.8 m in the section. Between 17.8 m and 19.8 m ∂13C values remain stable and a second positive shift of ~0.4 ‰ occurs between 19.5 to ~21 m, although the latter horizon is less clearly defined because of the lower resolution of the available ∂13C record (Brown et al., 2009) between 20 m. This discrete intervals and inflection points separating them can be now confidently dated by counting precession cycles relative to the C13n/C13r magnetochron boundary at Massignano. In particular, the onset of the first shift, which coincides with the onset of the increase of sedimentation rate, start at 34.1 Ma, concomitant with the onset of the ∂18O shift (Coxall et al., 2005), and culminates at 34.05 Ma. The platueau of stable 13C values spans 34.05 Ma to 33.93 Ma based on precession cycle counting. The second shift take about a further 120 kyr to accomplish, culminating at ~33.8, in near coincidence with the base of C13n, as observed in oceanic records (Coxall et al., 2005).

6. Conclusions

We have carried out a cyclostratigraphic analysis of the Massignano section – GSSP of the E/O boundary – and the nearby Massicore succession. Smilar to what already observed by other authors, spectral analyses of the Magnetic susceptibility, at both sites, and wt.%CaCO3, at Massignano GSSP, reveal the occurrence of an astronomical forcing signature in the analysed sedimentary successions. However, our interpretation significantly differs from previously published results and reconcile the Massignano GSSP astrochronology with the well-exstablished astrochronology available from oceani sites. Moreover, a fine-tuned cross correlation of the magnetic susceptibility records between the Massignano GSSP and Massicore allows to confidently correlate the two sites and identify the, otherwise loosely defined, C13n/C13r magnetochron boundary in the GSSP section..Filtering of the short eccentricity, obliquity and precessional components allows to establish a robust cyclochronology for the interval spanning magnetochron C16n2 to C13n. On this basis, we obtain the first integrated magnetostatigraphic and astrochronological age estimate of the E/O boundary from its type section, which is set at 34.014 Ma, therefore ~100 kyr than indirect estimates from oceanic sites.
The obtained astrochronology also allows to detect the major change in the oceanic saturation state and the consequent drowning of the CCD associated with the initial phase of the emplacement of a continental scale Antarctic Ice-sheet at the Eocene-Oligocene Transition in the Massignano section. The latter events, precedes the E/O boundary by ~100 kyr.

References

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Supplementary information

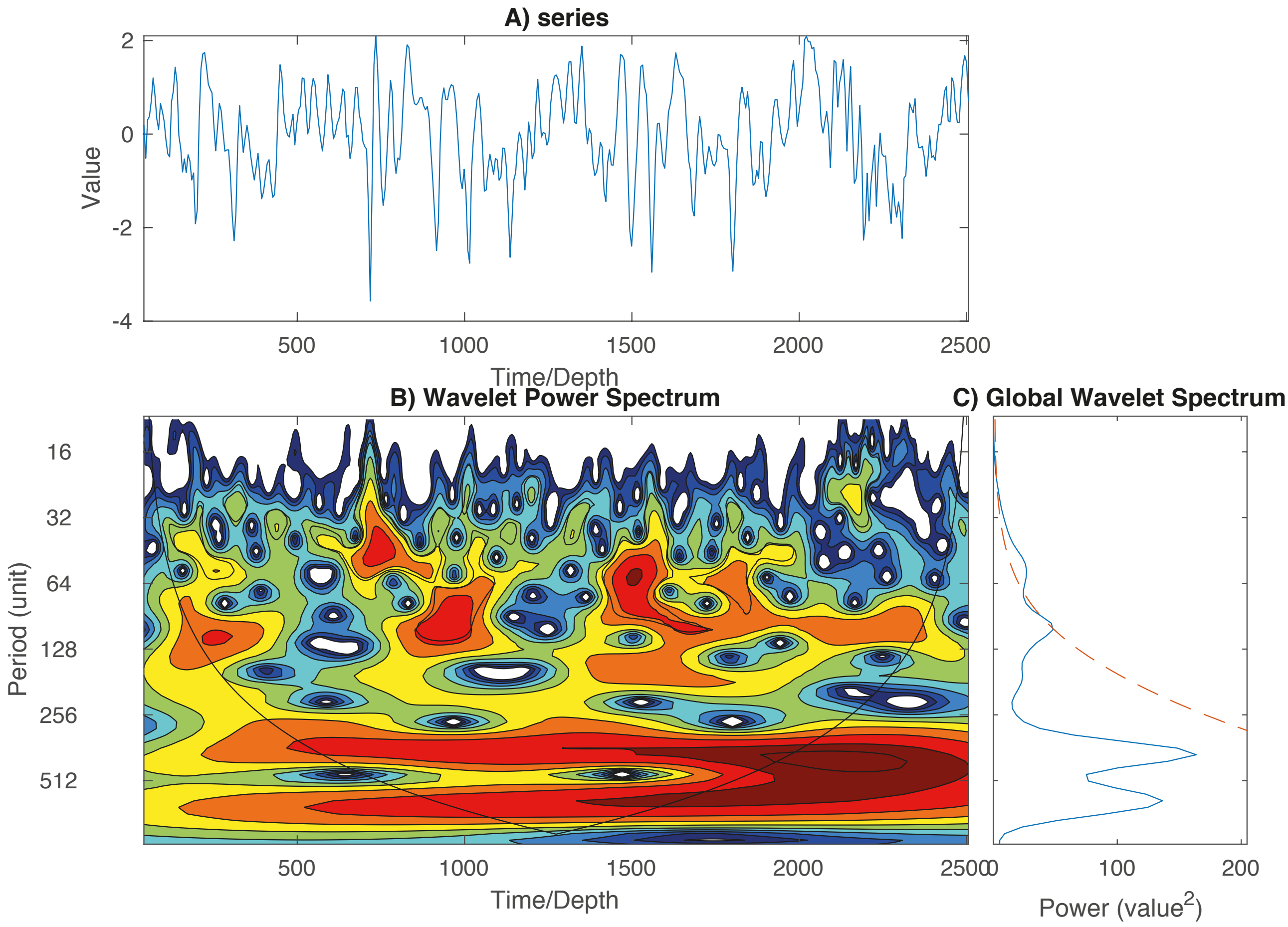

Figure S1