Synchronization of the astronomical time scales in the Early Toarcian: A link between anoxia, carbon-cycle perturbation, mass extinction and volcanism

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Abstract

The Late Pliensbachian-Early Toarcian is a pivotal time in the Mesozoic era, marked by pronounced carbon-isotope excursions, biotic crises and major climatic and oceanographic changes. Here we present new high-resolution carbon-isotope and magnetic-susceptibility measurements from an expanded hemipelagic Late Pliensbachian-Early Toarcian section from the Middle Atlas Basin (Morocco). Our new astronomical calibration allows the construction of an orbital time scale based on the 100-kyr eccentricity cycle. The Early Toarcian Polymorphum Zone contains 10 to 10.5 repetitions of the 100-kyr eccentricity both in the carbon-isotope and the magnetic-susceptibility data, leading to an average duration of 1.00 ± 0.08 myr. We also show that the Late Pliensbachian-Early Toarcian global carbon-cycle perturbation has an average duration of 0.24 ± 0.02 myr. These durations are comparable to previous astrochronological time scales provided for this time interval in the most complete sections of the Tethyan area, and longer than what has been provided in condensed sections. Anchoring this framework on published radiometric ages and astrochronological time scales, we estimate that the carbon-cycle perturbation of the Late Pliensbachian-Early Toarcian corresponds with the early phase of the Karoo and Chonke Aike large igneous provinces. Likewise, our new age constraints confirm that the Toarcian oceanic anoxic event is synchronous to the main phase of the Ferrar volcanic activity. Thus, these successive and short phases of the volcanic activity may have been at the origin of the successive phases of the mass extinctions observed in marine biotas in the Pliensbachian and Toarcian times.

Keywords:

Astrochronology; Toarcian; carbon cycle; Middle Atlas; oceanic anoxic events

1. Introduction

The Early Toarcian (184.15 – 174.1 Ma) was a time of global warming events (Dera et al., 2011), mass extinctions (Little and Benton, 1995), and pronounced negative carbon-isotope excursions recorded in marine carbonates and organic matter, brachiopods, biomarkers and fossil wood (Hesselbo et al., 2007; Suan et al., 2008a; Ait-Itto et al., 2017). These events coincide with carbonate production demises (Bassoullet and Baudin, 1994; Wilmsen and Neuweiler, 2008) and widespread oceanic anoxia (Jenkyns, 1988; Hesselbo et al., 2007).

Although large amounts of data have been produced, the timing and rhythms of the environmental perturbations are still debated, leading to controversies on the mechanisms at the onset of the climatic changes in the Early Toarcian (e.g. Kemp et al., 2005; Suan et al., 2008b). For instance, Martinez et al (2017) assess the duration of Pliensbachian-Toarcian event (P-To event) at 0.18 to 0.27 myr, while in the Peniche section (Lusitanian Basin, Portugal) the duration of this event is evaluated as 0.05 myr (Suan et al., 2008b). Similarly, the estimates of duration of the Polymorphum Zone vary from 90 kyr to 1.15 myr (Matiolli and Pittet, 2004; Suan et al., 2008b, Boulila et al., 2014; Huang and Hesselbo, 2014; Ruebsam et al., 2014; Martinez et al., 2017). The main reason of these differences is the occurrence of four discontinuity events identified by correlations of $\delta^{13}C$ and sedimentological features throughout the Tethyan margins, which are due to changes in the sea level observed in the earliest Toarcian (Pittet et al., 2014). The section studied here in Issouka, Morocco, is expanded compared to the sedimentary series from the northern Tethyan margin. It provides the opportunity to fill the gap in the time scale of the Toarcian Stage and to establish a detailed chronology of the succession of the environmental disturbances occurring in the Early Toarcian.

2. Geological setting

The geological history of Morocco was influenced by two important events, starting in the early Mesozoic with the opening of the north Atlantic and western Tethys and the collision of Africa and Europe during the middle Cenozoic (Michard, 1976). These events led to the formation of fault-bounded basins, which are made up of several smaller depocenters, separated by synsedimentary highs (Studer and Du Dresnay, 1980). The Middle Atlas is one of these small fault-bounded basins (Fig. 1). It constitutes a part of a Meso-Cenozoic intracontinental chain, namely the Moroccan Atlas (Michard, 1976). The Middle Atlas of Morocco is structurally dominated by four NE–SW trending anticlines and is mainly constituted of Lower and Middle Jurassic formations (Du Dresnay, 1971). The basin is bounded by the Saïs Plain and the front of the Rifian Nappes in the North, by the Guercif Basin in the northeast, by the Moulouya Plain to the southeast, and by the Hercynian Central Massif in the West.

The Middle Atlas Basin is deep in the center and shallows towards the northern and southern basin margins (Du Dresnay, 1971). The study area during the Early Toarcian was located at a palaeolatitude of ~20°N (Bassoulet et al., 1993) (Fig. 1A). The sedimentary evolution and palaeogeographic differentiation is controlled by tectonic activity, combined with the rate of sedimentation and global eustatic variations (Wilmsen and Neuweiler, 2008). The rapid transition from shallow marine carbonates to hemipelagic marls has been taken to reflect a major deepening phase across the entire Middle and High Atlas area (Wilmsen and Neuweiler, 2008). The Pliensbachian–Toarcian transition coincides with a dislocation of the Lower Jurassic carbonate platform (Lachkar et al., 2009; Ait Addi and Chafiki, 2013) with Toarcian deposits dominated by marls lying upon Upper Pliensbachian shallow marine limestones and calcareous marls. This drowning episode is linked to the eustatic sea-level rise of the Early Toarcian described in Europe and Africa (e.g. Hallam, 1997).

The biostratigraphy in the Middle Atlas has been established with ammonites (El Hammichi et al., 2008) with further biostratigraphic data provided by benthic foraminifera (Bejjaji et al., 2010). The ammonite zonation in the Issouka section is based on the Mediterranean zonation. Notably, the ammonites *Emaciaticeras emaciatum* of the Emaciatum Zone, *Dactylioceras polymorphum* of the Toarcian Polymorphum Zone and *Hildaites* in the Semicelatum Zone have been identified (e.g. El Hammichi et al., 2008). Furthermore, the occurrence of the benthic foraminifera *Lenticulina sublaevis* in the Issouka section is correlated by Bejjaji et al. (2010) to the Emaciatum ammonite zone of the Pliensbachian, whilst *Lenticulina bochardi* and *Lenticulina toarcense* are correlated with the Toarcian Polymorphum Zone and *Lenticulina obonensis* with the Serpentinus Zone.

The Issouka section is situated near the village of Issouka, ~25 km southwest of Immouzer Marmoucha, in the Middle Atlas (N33° 26’ 55.56”; W4° 20’ 33.83”; Fig. 1). The section begins with centimeter thick limestone–marl alternations (Fig. 2). The limestone beds contain a rich ammonite fauna, with also belemnites, echinoids and brachiopods. Foraminifera suggested a Late Pliensbachian age (Bejjaji et al., 2010; Fig. 2A). The early Toarcian succession starts with green marls and marl–limestone alternations, rich in foraminifera, belemnites, echinoids and gastropods. The Toarcian deposits are generally hemipelagic and correspond to deep marine environments (Bejjaji et al., 2010; Fig. 2B).

3. Material and methods

A total of 430 bulk-rock samples were collected with an even sample distance of 10 cm in the Issouka section. The samples were recovered from up to 15 cm below the surface, to minimize the effects of surface weathering. The sampled interval encompasses the end of the Pliensbachian Stage to the lowermost part of the Levisoni ammonite Zone. Such a range allows the Polymorphum Zone to be entirely sampled. The bulk-rock samples were then powdered using a metal ring grinder and analyzed for stables isotopes, magnetic susceptibility and calcium carbonate contents.

3.1. Carbon isotopes

A total of 430 samples were analyzed for stable isotopes at the University of Plymouth. Using 200 to 300 micrograms of carbonate, stable isotope data were generated on a VG Optima mass spectrometer with a Gilson autosampler. Isotope ratios were calibrated using NBS19 standards and are given in δ notation relative to the Vienna Pee Dee Belemnite (VPDB). Reproducibility was generally better than 0.1 ‰ for samples and standard material.

3.2. Magnetic susceptibility

The magnetic susceptibility (MS) of the 430 powdered samples was measured with a Kappabridge KLY-3. The samples are placed in small plastic cubes of 10 cm^3 and then introduced inside the instrument using the “pick-up” unit. We measured the cube empty and then with samples for blank correction. The blank-corrected MS values are normalized to their mass and volume. The resulting values are reported as mass-specific MS ($m^3.kg^{-1}$).

3.3. Calcium carbonate content

The samples were analyzed for their calcium carbonate content using a Bernard calcimeter at the Geosciences and Environment Laboratory, Cadi Ayyad University. The values are given with a precision between 1 and 5% (Lamas et al., 2005).

3.4. Spectral analysis

Prior to spectral analysis, the long-term trend of both series was measured and subtracted from the series to ensure stationarity. The detrend procedures removed the high powers in the frequencies close to 0, while not creating new spectral peaks in the low frequencies (see Vaughan et al., 2015). Best-fit linear trend and LOWESS smoothing curves (Cleveland et al., 1979) were applied. The exact coefficients depend on each of the series and are detailed in the results. Following the removal of this long-term trend, the multi-taper spectral analyses, using three 2π prolate tapers (2π-MTM) with robust red-noise modelling (Mann and Lees, 1996) modified in Meyers (2014) were applied to evaluate lithological cycles as a possible record of astronomically forced sedimentation following the LOWSPEC approach (Meyers, 2012). The significance levels were then calculated assuming a chi-square distribution of the spectral background. We used the time-frequency weighted fast Fourier transforms (T-F WFFT; Martinez et al., 2015) to characterize the evolution of the periods through the sedimentary series. Taner low-pass and band-pass filters (Taner, 2003) were then applied to isolate each signal interpreted as an orbital forcing and calculate the duration of the Polymorphum Zone by cycle counting. Orbital tuning procedures are then used to anchor the sedimentary cycles to their corresponding orbital periods, allowing depth-time conversions to be done. Durations are then estimated by calculating the difference of relative ages. Error margins of each of the time intervals include the difference between the average and the calculated durations and the uncertainty in the orbital frequencies.

4. Results

4.1. Carbonate carbon isotopes

The carbon-isotope profile of the Issouka section shows relatively high values in the Pliensbachian part of the section, ranging from +1.7‰ to +2.7‰ (Fig. 3A). From 5 m to 5.6 m, the $\delta^{13}C$ decreases from 2.5‰ to -0.6‰. This abrupt decrease of 3‰ in the $\delta^{13}C$ observed at the base of the Toarcian is related to the Pliensbachian-Toarcian event (P-To event; Suan et al., 2008a; Ait-Itto et al., 2017). The $\delta^{13}C$ values then remain low from 5 m to 23 m. In this interval, the values show gentle fluctuations from 5 to 17 m. At 17 m, the $\delta^{13}C$ abruptly increase by 1‰ before they gently decrease until 23 m to -2‰. The values then progressively increase from 23 m to 30 m, changing from -2‰ to 1‰. Above 30 m to the top of the section, the values slightly increase from 1 to 2‰.

4.2. Magnetic susceptibility

The magnetic susceptibility curve (Fig. 3E) firstly shows from the base of the series to level 5.1 m low values, ranging from $9.65x10^{-9}$ to $3.15x10^{-8}$ $m^3.kg^{-1}$. This interval corresponds to the limestone-dominated part of the formation of Pliensbachian age. From 5.2 m to the top of the series, MS values increase with an average value $1.04x10^{-7}$ $m^3.kg^{-1}$. The interval from 27 m to 35 m shows lower values of the MS in a more carbonated interval. Calcium carbonate content and MS values display a strong inverse correlation (r = -0.91, Fig. 4), indicating that the lithology mainly controls the MS variations.

4.3. Calcium carbonate content

The carbonate content series (Fig. 3D) firstly show high values (>80% on average) from the base of the series to 5.1 m, in the interval of the limestone beds of the Pliensbachian. From 5.2

m to 8.4 m, the values rapidly decrease from 91% to 8.6%. From 5.2 m to 18 m, the $CaCO_3$ values remain low with average values around 22%. The transition between the first to the second interval is more progressive than observed in the $\delta^{13}C$ series (Fig. 3A). From 18 m to 42.9 m $CaCO_3$ series show high-amplitude cycles and high-frequency fluctuations from 60% and 20% linked to the limestone-marl alternations (Fig. 3D).

4.4. Spectral analyses

4.4.1. Carbon-isotope signal

The $\delta^{13}C$ shows a rapid decrease at 5.2 m, and a rapid increase at 16.6 m (Fig. 3A). The series was stationarized using a best-fit linear trend from 0 to 5.1 m, a LOWESS regression with a coefficient of 0.6 from 5.2 to 16.5 m and a LOWESS regression with a coefficient of 0.3 from 16.6 to 42.9 m. The LOWESS coefficients have been chosen in such a way that they approximatively cover the same length of the section (i.e. ~7 m on average), which represents *ca.* 20% of the Toarcian part. This choice decreased the high powers at frequencies near 0, while not creating spurious spectral peaks in the low frequencies (Vaughan et al., 2015). The three subseries were then standardized (average = 0, standard deviation = 1) and stacked. Two points at 11.7 m and 12 m showing outstandingly low values when detrending may bias the spectrum in the high frequencies and have been removed from the series before detrending. The evolutive spectrum of the $\delta^{13}C$ series shows a high-power spectral band in the low frequencies evolving having a period of 4.1 to 4.2 m from the base of the series to level 24 m (Fig. 3C). The period of this band then decreases to 3 m, from level 24 m to level 31 m, and stabilizes at 3 m from level 31 m to the top of the series. These changes in the period of the ~4-m peak likely reflects variations in the sedimentation rate. These distort the sedimentary record of the orbital cycles by decreasing the *p*-value of the low frequency and flattening the spectrum at high frequencies (Weedon, 2003; Kemp, 2016; Martinez et al., 2016). We thus decided to analyze the frequency content of two sub-intervals of the series in which variations in the sedimentation rate are limited. The range of each of the sub-intervals is given in Fig. 3C. We compared the frequencies of the carbon isotopes in each interval with the orbital frequencies calculated for the Toarcian (Waltham, 2015), using the average spectral misfit (ASM; Meyers and Sageman, 2007). The ASM method compares the sedimentary frequencies converted into time to the orbital frequencies and provides a quantitative assessment on the most likely sedimentation rate in each sub-interval (see supplementary materials).

Spectra of Interval 1, from levels 0 to 31 m, show significant periods above the 99% confidence level (CL) at 4.2 m (frequency: 0.2404 cycles.m^{-1}), and above the 95% CL at 1.2 m (frequency: 0.8013 cycles.m^{-1}), 0.83 m (frequency: 1.202 cycles.m^{-1}), and 0.31 m (Fig. 5A, C). Spectra of Interval 2, from levels 24 m to the top of the series show significant peaks above the 95% CL at 3.2 m (frequency: 0.3158 cycles.m^{-1}), 0.63 m (1.579 cycles.m^{-1}) and 0.33 m (Fig. 5B, D).

As noted above, various astrochronological frameworks estimate the duration of the Polymorphum Zone from 0.09 myr to 1.15 myr (Mattioli and Pittet, 2004; Suan et al., 2008b; Huang and Hesselbo, 2014; Boulila et al., 2014; Martinez et al., 2017; Boulila and Hinnov, 2017), implying a sedimentation rate varying from 400 m/myr to 31 m/myr. When converting m-cycles to time-cycles, the peaks at ~0.3 m have periods below the Milankovitch band whatever the sedimentation rate considered, so were excluded from the ASM analysis. Testing ASM over 500 sedimentation rates ranging from 0.4 cm/kyr to 40 cm/kyr leads to a most likely sedimentation rate of 3.9 cm/kyr (39 m/myr) in Interval 1, and to a most likely sedimentation rate of 3.2 cm/kyr (32 m/myr) in Interval 2 (Fig. 5E, F). The H0-significance level at the most likely sedimentation rate is below the critical significance level below which we can consider without ambiguity these spectra reflect an orbital forcing. In Interval 1, peaks at 4.2 m, 1.2 m and 0.83 m are respectively due to the 100-kyr eccentricity, the obliquity and the precession cycles. Notice than the peak of 1.2 m leads to an obliquity period which is shorter than expected in the theory (here 29.4 kyr vs. 37.5 kyr in Waltham, 2015). In Interval 2, peaks at 3.2 m and 0.63 m are respectively due to the 100-kyr eccentricity and the precession cycles. In addition, the peak at 0.33 m has a mean period of 10 kyr, which corresponds to the semi-precession, the first harmonic of the precession (Berger et al., 2006).

The evolutive spectral analysis indicates the 100-kyr cycle is the most continuous throughout the studied series (Fig. 3C). We filtered the 100-kyr eccentricity recorded in the $\delta^{13}C$ series and used it as target cycle for calibrating the series in time. We filtered the 100-kyr cycle using a Taner low-pass filter with a frequency cut of 0.3953 cycles.m^{-1} and a roll-off rate of 10^{36}. The output filter indicates that the Polymorphum Zone contains 10 repetitions of the 100-kyr eccentricity cycle (Fig. 3B).

4.4.2. Magnetic susceptibility

The MS series is marked by a rapid increase of values from 5.0 m to 6.8 m. The trend of the series is then gentler. The series was stationarized using a best-fit linear regression from 0 to 5.2 m and a LOWESS smoothing with a coefficient of 0.2 in the remainder of the series, which represents 7.5 m of the section. The two subseries were then standardized (average = 0, standard deviation = 1) and stacked. The evolutive spectrum of the MS series shows a band in the low frequencies evolving from 3.1 m to 3.7 m in the lower part of the series, from the base of the series to level 20 m (Fig. 3G). Then, this period decreases to 2.9 m from level 26 m to the top of the series. 2π-MTM spectra have been generated from Interval 1 (from the base of the series to level 26 m), and from Interval 2 (from 21 m to the top of the series) (Fig. 6). Spectra of Interval 1 show spectral peaks over the 99% CL at 3.3 m and 0.38 m, and peaks over the 95% CL at 0.81 m and 0.23 m (Fig. 6A, C). Spectra of Interval 2 show peaks over the 99% CL at 2.9 m, 2.0 m, 0.27 m and 0.22 m, and a peak exceeding the 95% CL at 1.0 m (Fig. 6B, D).

Assuming from ASM applied on the $\delta^{13}C$ spectra that Interval 1 has a mean sedimentation rate of 39 m/myr, the peaks of 3.3 m, 0.81 m and 0.38 m are attributed to the 100-kyr eccentricity, the precession and the semi-precession, respectively. Assuming from ASM that Interval 2 has a mean sedimentation rate of 32 m/myr, the peak of 2.9 m, 1.0 m and 0.27 m are respectively attributed to the 100-kyr eccentricity, the obliquity and the semi-precession (Fig. 6).

In Interval 1, the period of the 100-kyr cycle is lower in the MS series than in the $\delta^{13}C$. On the evolutive spectral analyses, this is particularly obvious in the first 10 m of the series, when the lithology evolves from the limestones of the Pliensbachian to the marls of the Toarcian (Fig. 3). The 100-kyr eccentricity recorded in the MS series was isolated using a Taner low-pass filter with a frequency cut of 0.4070 cycles.m^{-1} and a roll-off rate of 10^{36} (Fig. 3). The output filter indicates that the Polymorphum Zone clearly contains ~10.5 repetitions of the 100-kyr eccentricity cycle compared to the 10 repetitions observed in the $\delta^{13}C$ (Fig. 3).

5. Discussion

5.1. Astrochronology of the the Polymorphum Zone

The $\delta^{13}C$ and the MS signals both display 12 complete short eccentricity cycles along the studied section. In the astronomical models computed for the last 20 myr (Laskar et al., 2004), the average duration of 12 consecutive short eccentricity cycles is 1149 ± 63 kyr (2σ), so that the average duration of a short eccentricity cycle 95.8 ± 5.2 kyr (2σ). Assuming a constant sedimentation rate between two successive anchor points of the 100-kyr cycle obtained from the filters of the $\delta^{13}C$ and the MS signals, the durations calculated of the Polymorphum Zone range from 0.97 myr with the $\delta^{13}C$ signal, to 1.02 myr with the MS signal. In the spectra of the untuned series, the period of the 100-kyr cycle is longer in the $\delta^{13}C$ than in the MS (Figs. 3, 5, 6). The difference is particularly noticeable in the first 10 m (Fig. 3). Below level 5 m, the filter of 100-kyr cycle in the $\delta^{13}C$ is inversely correlated to the filter of the 100-kyr in the MS signal. After 5 m, i.e. after the start of the P-To event, the two filters are in phase. The limestone beds in the Pliensbachian of the atlasic basins originate from exports from the neritic environments, in which the $\delta^{13}C$ was higher than in pelagic environments (Wilmsen and Neuweiler, 2008). In the Pliensbachian, the $\delta^{13}C$ is higher in limestone beds. The P-To Event corresponds to a demise in the neritic carbonate production. Fluctuations in the $\delta^{13}C$ thus correspond to fluctuations in the pelagic production, which is usually higher during the deposit of marlier intervals, when detrital and nutrient increased the primary productivity (Mutterlose and Ruffell, 1999; Mattioli and Pittet, 2004). The demise of the carbonate platforms thus changed the phasing between the MS and the $\delta^{13}C$, which is a source of uncertainty in the calculation of the durations. Another change of phasing occurs at 28 m, where the $\delta^{13}C$ and the $CaCO_3$ content increase. As the phasing between the orbital configuration and the proxies is still unclear, we choose to retain the average duration of 1.00 ± 0.08 myr for the Polymorphum Zone (the uncertainty includes the age model and the duration of a short eccentricity period, see supplementary materials).

The spectrum of the calibrated $\delta^{13}C$ shows a high power at 96 kyr (expected when calibrated to the short eccentricity), 32.4 kyr (main obliquity), 24.1 and 19.7 kyr (precession), and 13.2 to 11.0 kyr (half-precession) (Fig. 7A). In addition, a peak exceeding the 95% confidence level appears at 400 kyr, which corresponds to the long-eccentricity cycle. The spectrum of the calibrated MS shows a high power at 95.7 kyr (expected), 65.5 kyr, 31.9 kyr (main obliquity), from 24.4 to 19.1 kyr (precession), and from 12.1 to 10.6 kyr (half precession) (Fig. 7B). In the $\delta^{13}C$ and MS signals, the precession cycle has slightly longer periods than expected in the theory (Waltham, 2015). This may be the consequence of a precession cycle missing per short eccentricity. In the astronomical solutions, the amplitude of the precession band is modulated by the 405-kyr and the 100-kyr eccentricity cycles, while the amplitude of the 100-kyr cycle is modulated by the 400-kyr cycle (Laskar et al., 2004). The Taner band-pass filter of the precession cycle in the $\delta^{13}C$ series was performed with frequency cuts of 3.583 x 10^{-2} cycles/kyr and 5.417 x 10^{-2} cycles/kyr, and a roll-off rate of 10^{36} (Fig. 8B, E). We calculated the amplitude modulation (AM) of the precession cycles using a Hilbert transform. The spectrum of the AM of the precession filter shows cycles at 340 kyr (near the 405-kyr eccentricity), and at 123 and 82.8 kyr (near the periods of 124 and 95 kyr of the short eccentricity) (Fig. 8F). We filtered the 100-kyr band of the AM of the precession filter using a Taner band-pass filter with frequency cuts of 6.250 x 10^{-3} cycles/kyr and 1.558 x 10^{-2} cycles/kyr and a roll-off rate of 10^{36} (Fig. 8F). The AM of this filter shows a cycle at 340 kyr (Fig. 8G). Similarly, the spectrum of the AM calculated on the direct filter of the 100-kyr band shows a cycle at 436 kyr (Fig. 8H). Thus, the AM of the precession and the 100-kyr eccentricity show similar patterns as expected in the astronomical models. The filters of the two bands shows 11 cycles of short eccentricity within the Polymorphum Zone (Fig. 8C), while the various filters of the 405-kyr cycles in the AM of the precession and the 100-kyr cycles show from 3 to 4 repetitions of the 405-kyr cycle (Fig. 8A, C, D). The difference between the direct filter and the filter of the AM is explained by the residence time of carbon in the ocean, which creates a delay in the response of the $\delta^{13}C$ to the orbital forcing (Laurin et al., 2017). In this context of hemipelagic sediments, with the limestone beds originating from exports from neritic environments, the difference may also be due to the change of the carbonate source.

The duration of the Polymorphum Zone from this study is longer than the duration of ~0.8 myr assessed in the Peniche section (Suan et al., 2008b; Huang and Hesselbo, 2014) and the Foum Tillicht section (Martinez et al., 2017). The correlation of these sections led to a duration of a composite Polymorphum Zone of 0.9-1.0 myr, which agrees with the duration calculated here. In addition, the duration calculated here is in close agreement with the duration estimated from Central Italy, in which 11 bundles of marl-limestone alternations have been related to the 100-kyr eccentricity cycle (Mattioli and Pittet, 2004).

The series of condensation affecting the Pliensbachian-Toarcian transition strongly affects the duration assessments in the Northern Tethyan margin. For instance, in the Paris Basin, the duration of the Tenuicostatum Zone (equivalent to Polymorphum) varies from 0.09 myr to 0.5 myr (Boulila et al., 2014; Ruebsam et al., 2014). Correlations of $\delta^{13}C$ curves indicate that these sections are affected by a series of condensation events, leading to an underestimation of the duration of the Tenuicostatum Zone (Pittet et al., 2014). Recently, Boulila and Hinnov (2017) suggested that the 100-kyr eccentricity cycles identified in Suan et al. (2008b) and Huang and Hesselbo (2014) are the record of the obliquity cycle. However, this would imply a hiatus of ~800 kyr in the middle of the Tenuicostatum Zone, which is not indicated in the $\delta^{13}C$ data (Pittet et al., 2014). In addition, detailed observations of the sedimentological pattern of Peniche indicate than these cycles correspond to bundles of 4-6 marl-limestone alternations, which is related to the hierarchy in between the short eccentricity and precession (Suan et al., 2008b). We thus retain here for the Peniche section the astrochronological models from Suan et al. (2008b) and Huang and Hesselbo (2014).

5.2 Duration of the P-To Event

The duration of the P-To event varies from ~50 kyr to 0.27 myr from various astrochronological models (Suan et al., 2008b; Huang and Hesselbo, 2014; Martinez et al., 2017). Uncertainties are due to the condensation event often observed at the Pliensbachian-Toarcian boundary (Pittet et al., 2014) and to the difficulty in defining the upper boundary of the P-To event (Martinez et al., 2017). The P-To event indeed starts with an abrupt decrease of 2 to 3‰ the $\delta^{13}C$ and change in lithology from carbonated to detrital sediment (Suan et al., 2008a; Bodin et al., 2010). Then, the $\delta^{13}C$ values gently increase, making the definition of an upper limit of the P-To event problematic. Martinez et al. (2017) defined two options to define the upper boundary of the P-To event: (i) the end of the decrease of the $\delta^{13}C$ and $CaCO_3$ values; (ii) the local increase of the

$\delta^{13}C$ values in the lower part of the Polymorphum Zone, corresponding to a maximum of the filter of the 405-kyr band in the $\delta^{13}C$. In the Issouka section, the filter of the 405-kyr band was calculated on the calibrated series (high frequency cut: 0.005833 cycles/kyr; roll-off rate: 10^{36}) and converted into depths shows that this maximum is at 13.1 m (Fig. 9). We suggest using this marker as the end of the P-To event, as it can be observed both in the Central High Atlas and the Middle Atlas. From the $\delta^{13}C$ and the MS age models, the duration of the P-To event as defined here varies from 0.23 to 0.25 myr, with an average duration of 0.24 ± 0.02 myr (this uncertainty takes into account the uncertainty of the age model and the uncertainty of the period of the eccentricity, see supplementary materials). These durations are in agreement with Option 1 from the Foum Tillicht section, which vary from 0.25 to 0.29 myr, with an average duration of 0.27 myr (Martinez et al., 2017). This duration of the P-To event appears stable in Moroccan sections, ranging from 0.23 to 0.29 myr.

5.3. A synthetic astrochronology for the Tethyan area in the Early Toarcian

The Polymorphum Zone at Issouka shows 10 to 10.5 repetitions of the 100-kyr eccentricity cycles. In comparison, the sedimentary records of Foum Tillicht and Peniche show a total of eight 100-kyr eccentricity cycles for the Polymorphum Zone. Lithological patterns in the Umbria-Marche Basin tend to indicate that the Polymorphum Zone contains ten to eleven repetitions of 100-kyr cycle (Mattioli and Pittet, 2004). Four discontinuities identified in the Pliensbachian-Toarcian transition have affected the completeness of the sedimentary record in the Foum Tillicht and the Peniche sections. In particular, at Peniche, the Pliensbachian-Toarcian transition appears condensed, while in Foum Tillicht the top of Polymorphum is missing (Martinez et al., 2017). In Issouka, Foum Tillicht and Peniche, $\delta^{13}C$ has been measured at a high resolution and astrochronologies have been produced, making it possible to correlate the sections at a Milankovitch scale.

Based on the astrochronological frameworks produced in this study and in Huang and Hesselbo (2014) and Martinez et al. (2017), we can correlate these three sections at the eccentricity scale (Fig. 9). Radiometric ages have been anchored on stratigraphic ages at the Triassic-Jurassic boundary, in the Hettangian and the Sinemurian (Ruhl et al., 2016). A U-Pb age has been proposed for the uppermost part of the Tenuicostatum Zone at 183.22 ± 0.26 Ma in Southern Peru (Sell et al., 2014). The lack of intercalibration with astrochronology makes it difficult to anchor it on our time scale. Conversely, the Triassic-Jurassic boundary have been bracketed at 201.36 ± 0.17 Ma with U-Pb ages from the Pucara Basin (Peru) and the New York Canyon (Nevada, USA), recalibrated applying version 3.0 of EARTHTIME tracer (Wotzlaw et al., 2014). The duration of the interval from the base of the Jurassic to the base of the Toarcian have been assessed at 17.21 myr (Ikeda and Tada, 2014), which matches with the time scale suggested in Ruhl et al. (2016) with an uncertainty of ± one 405-kyr cycle. It positions the base of the Toarcian at 184.15 ± 0.58 Ma. The uncertainty retained here corresponds to the sum of uncertainties of astrochronology and radiochronology.

Other ages are as follows (see also supplementary materials for details of the calculations):

- The average duration of the P-To event is 0.24 ± 0.02 myr, positioning the top of the P-To event at 183.91 ± 0.60 myr,
- The average duration of the Tenuicostatum/Polymorphum Zone is 1.00 ± 0.08 myr, positioning the top of Tenuicostatum/Polymorphum at 183.15 ± 0.66 Ma. Notice that this age fits with the age of Sell et al. (2014) of 183.22 ± 0.26 Ma for the uppermost part of the Tenuicostatum Zone,
- The base of the T-OAE occurs 0.03 myr after the end of the Polymorphum Zone (Huang and Hesselbo, 2014; Fig. 9), i.e. 183.12 ± 0.66 Ma,

- The T-OAE encompasses 11 short-eccentricity cycles (Suan et al., 2008b; Huang and Hesselbo, 2014; Thibault et al., 2018), corresponding to a duration of 1.05 ± 0.06 myr (Fig. 9). The top of the T-OAE is thus dated here at 182.07 ± 0.72 Ma,

5.4. Origins of P-To and T-OAE disturbances

The large negative CIEs observed in the Early Toarcian, the P-To event and the T-OAE, imply the injection of large amount of light carbon in the oceanic system (Suan et al., 2015). This has been interpreted as dissociation of methane hydrate, maybe orbitally paced (Kemp et al., 2005), or production of thermogenic methane due to volcanic intrusion during the Karoo-Ferrar activity (Svensen et al., 2007). The long duration of the T-OAE (Suan et al., 2008b; Huang and Hesselbo, 2014) implies that the amount of methane needed to maintain the negative excursion for such a long time would exceed the volume of gas hydrate reservoir (Suan et al., 2008b). In addition, the interval of the T-OAE display a positive excursion in Hg/TOC, associated with a volcanic activity (Percival et al., 2015). CA-ID-TIMS U-Pb ages indicate that the Ferrar province activity occurred from 182.779 ± 0.033 Ma and lasted 349 ± 49 kyr (Burgess et al., 2015). These ages fall in the range of the ages assessed here for the T-OAE (183.12 ± 0.66 Ma to 182.07 ± 0.72 Ma; Fig. 9). All these observations tend to favour the crucial role of the Karoo-Ferrar activity on the inception of the T-OAE. Hg/TOC data from Yorkshire and the Peniche sections show a positive excursion within the P-To event, which tend to indicate the concomitance between the P-To event and volcanic activity. The P-To event started 184.15 ± 0.58 Ma and ended at 183.91 ± 0.60 Ma (Fig. 9), so that the P-To event appears significantly older than the activity of the Ferrar province. Dating of the early phase of the Karoo province tends to indicate that the Karoo province started earlier than the Ferrar (Burgess et al., 2015; Moulin et al., 2017). Notably the oldest $^{40}Ar/^{39}Ar$ ages of the Karoo activity have been found in the southern part of the Barkly East Formation (South Africa), within the Omega and the

Moshesh's Ford units (Moulin et al., 2017 and references therein). Other ages older than 183 Ma have been reported in the Northern part of the Chonke Aike LIP (South America) in the Rio Negro Province and in the eastern part of the Chubut Province (Féraud et al., 1999). The location and the thicknesses of the formations in which these older $^{40}Ar/^{39}Ar$ and and U/Pb ages have been provided are, to our knowledge, much more limited than that of the main phase of the Karoo-Ferrar activity (~183 Ma). While this main phase is likely to be responsible for the inception of the T-OAE, limited volcanic activities in the early phase of the Karoo and Chonke Aike LIP may have affected the environmental and ecological perturbations recorded at the Pliensbachian-Toarcian boundary.

6. Conclusions

The carbon isotope and MS variations in the Late Pliensbachian-Early Toarcian, performed in the expanded hemipelagic in Issouka section from the Middle Atlas Basin, Morocco, reveal superposed frequencies consistent with Milankovitch forcing (eccentricity, obliquity, and precession). The Polymorphum Zone contains 10 to 10.5 repetitions of the 100-kyr eccentricity cycle, so that its duration is assessed here at 1.00 ± 0.08 myr. The duration of the P-To event is in addition assessed at 0.24 ± 0.02 myr. The recognition of the 100-kyr and the 405-kyr eccentricity enabled us to establish a stratigraphic framework between the Northern and the Southern Tethyan margins. Anchoring this framework on published radiometric ages and astrochronological time scales, we could estimate the age of the base of the Toarcian as 184.15 ± 0.58 Ma, the top of the P-To event as 183.91 ± 0.60 Ma, the base of the Toarcian OAE as 183.12 ± 0.66 Ma, and the top of the Toarcian OAE as 182.07 ± 0.72 Ma. The age of the Toarcian OAE fits with the ages published for the Ferrar volcanic activity. Conversely, the age of the P-To event seems to correspond with early phase of the Karoo and Chonke Aike activity. Thus, the successive and short phases of the volcanic activity of the Chonke Aike, Karoo and

Ferrar provinces may have been the smoking gun of the successive phases of the mass extinction observed in marine biotas in the Pliensbachian and Toarcian times.

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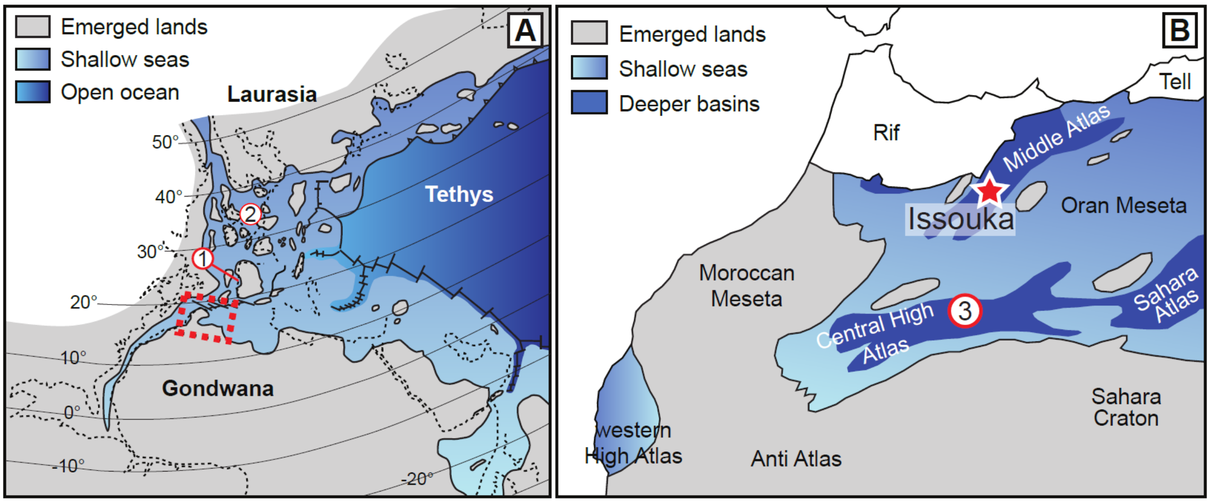


Fig. 1. Geological setting of the Issouka section. **A.** Palaeogeographic map of the western Tethys during the Early Jurassic. The red dash rectangle shows the limit of the second map. Label "1" indicates the location of the Peniche section. Label "2" indicates the location of Yorkshire area. **B.** Geographical map of Morocco and western Algeria showing the main geological provinces and the location of the Issouka section within the Middle Atlas. Label "3" indicates the location of the Foum Tillicht section (maps from Bodin et al., 2010).

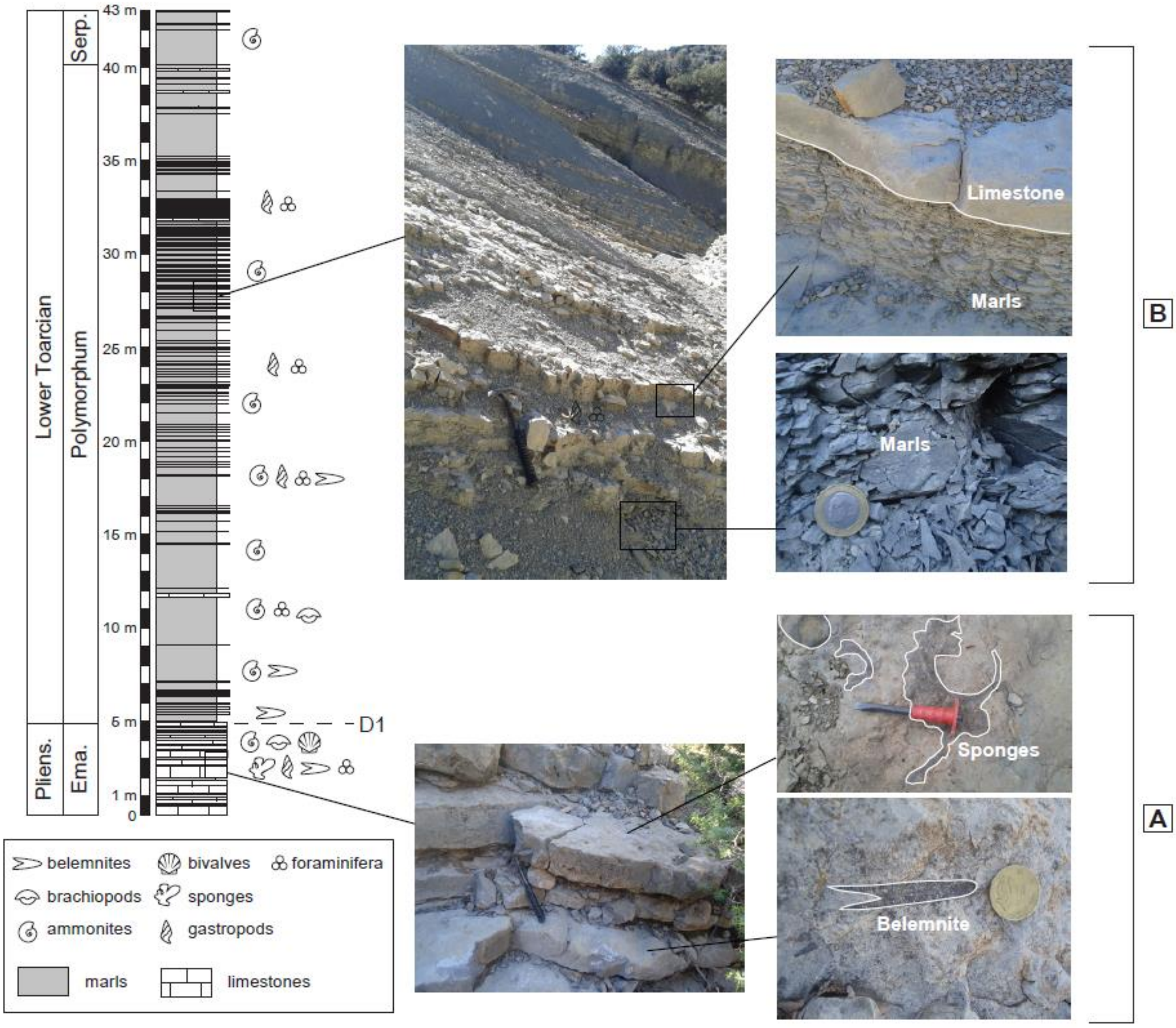


Fig. 2. The different facies in the Issouka section. **A.** Limestone of the late Pliensbachian with fauna (belemnites, sponges and brachiopods). **B.** The Lower Toarcian, characterized by grey marls and limestone intercalations.

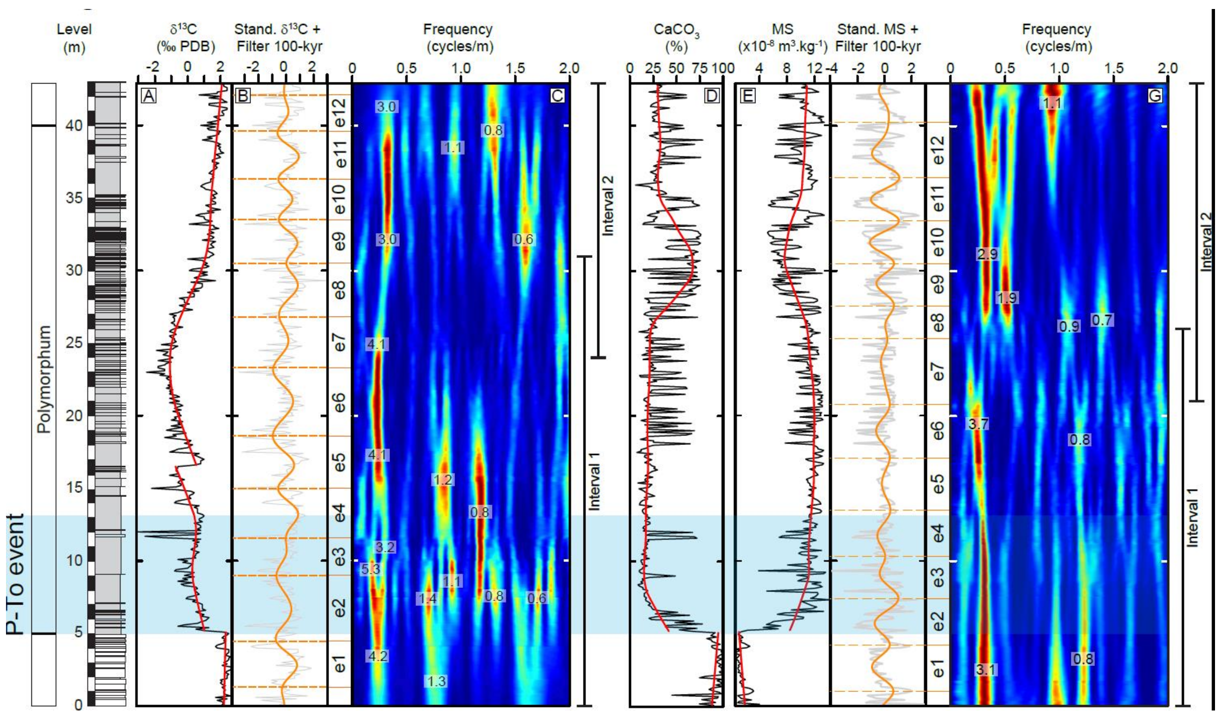


Fig. 3. Raw data, spectrograms and filters of the 100-kyr eccentricity band of the carbon isotope ($\delta^{13}C$) and magnetic susceptibility (MS) signals. **A.** Raw $\delta^{13}C$ signal (in black) with long-term trend (in red). **B.** Standardised $\delta^{13}C$ signal (in grey) with the filter of the 100-kyr eccentricity (in orange). **C.** Spectrogram of the $\delta^{13}C$ signal performed with 15-m-width windows. **D.** Raw $CaCO_3$ signal (in black) with long-term trend (in red). **E.** Raw MS signal (in black) with long-term trend (in red). **F.** Standardised MS signal (in grey) with the filter of the 100-kyr eccentricity (in orange). **G.** Spectrogram of the MS signal performed with 15-m-width windows.

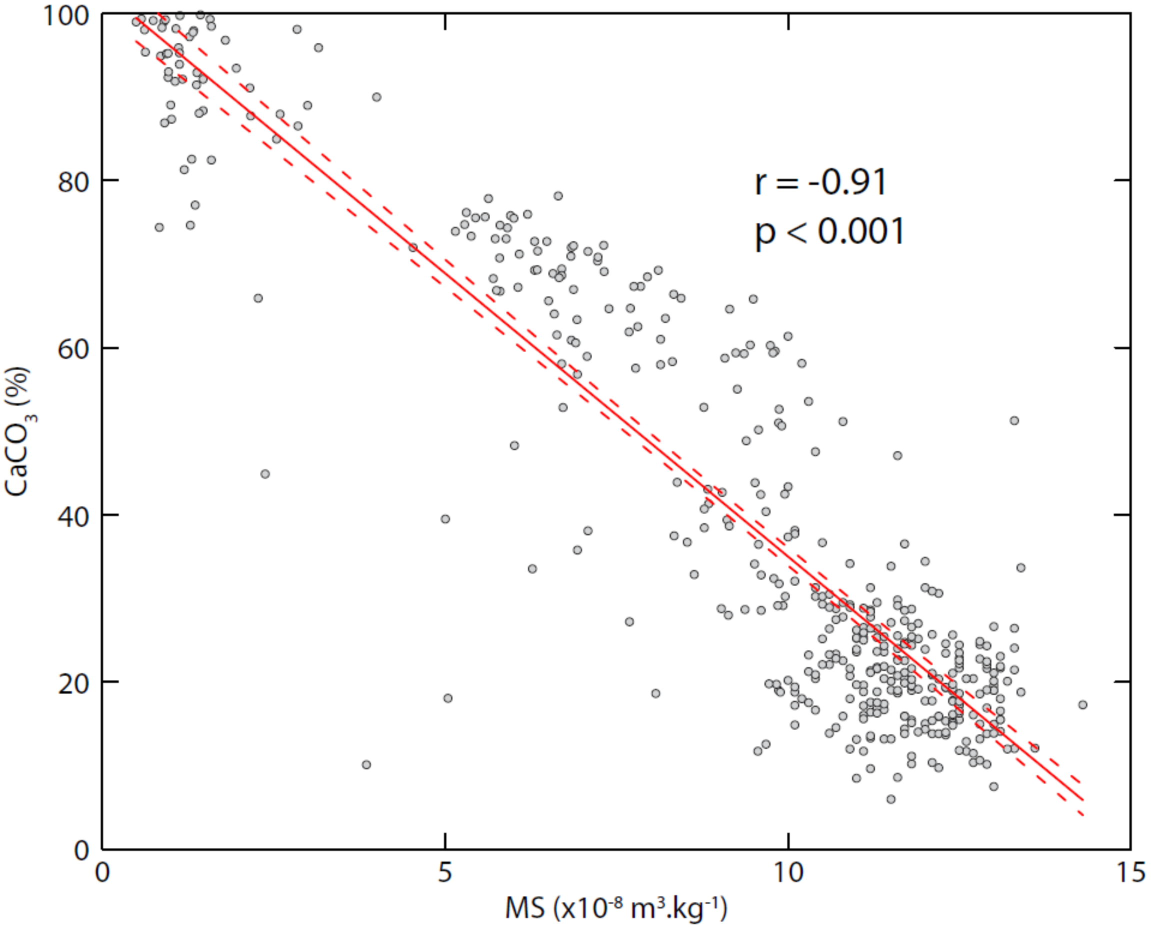


Fig. 4. Cross-plot of the magnetic susceptibility (MS) versus calcium carbonate content ($CaCO_3$). The full red line is the best-fit linear regression, while dash lines are the 95% confidence intervals of the linear regression. *r* indicates the coefficient correlation, and *p* is the *p*-value of the correlation.

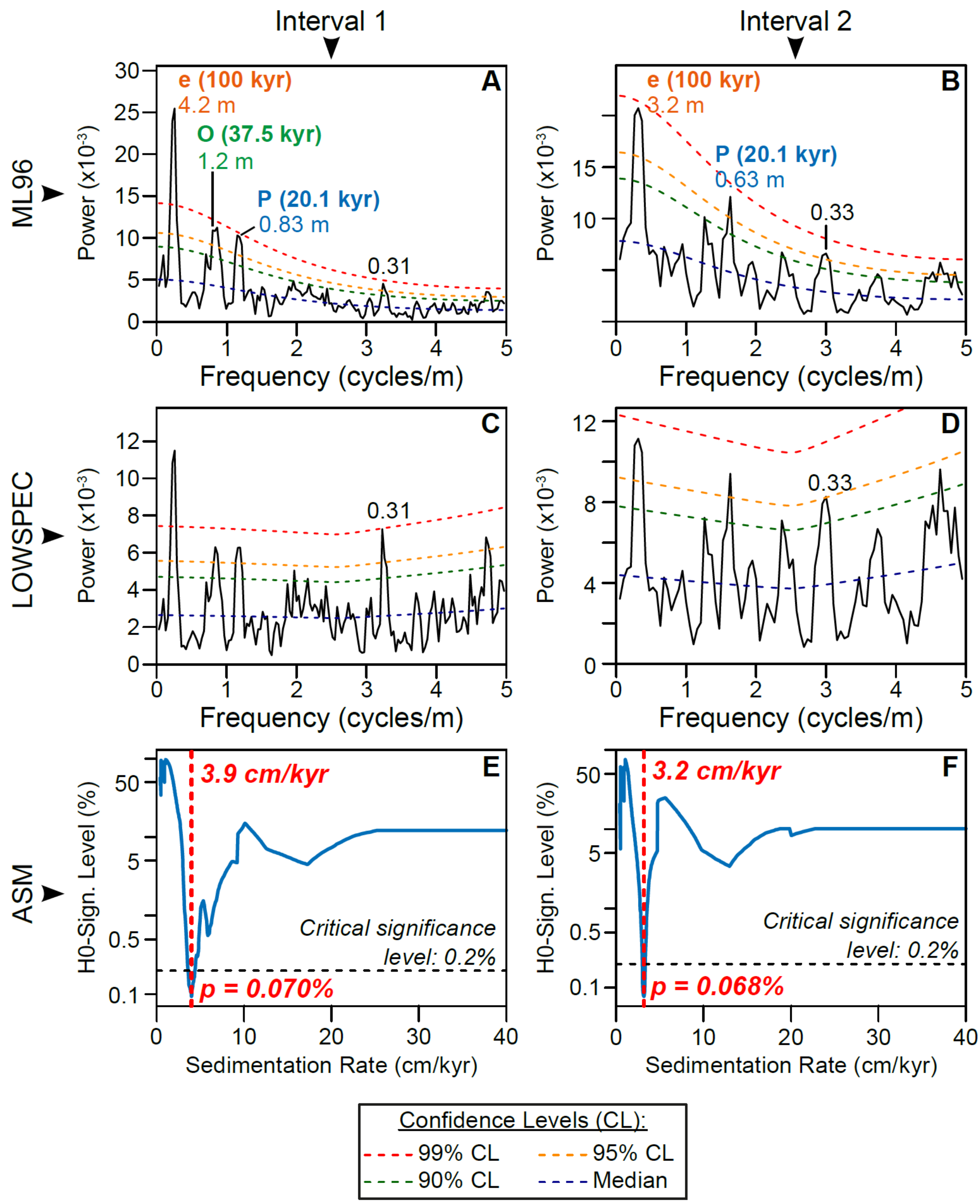


Fig. 5. 2π-MTM spectra and ASM results of the $\delta^{13}C$ series. **A. and B.** Spectra of intervals 1 and 2 with confidence levels calculated with the Mann and Lees (1996) method (ML96) with a Tukey's endpoint rule (Meyers, 2014). **C. and D.** Spectra of intervals 1 and 2 with confidence levels calculated with the LOWSPEC method (Meyers, 2012). **E. and F.** H0 significance levels from the ASM applied on intervals 1 and 2. The red dashed line indicates the sedimentation rate for which the sedimentary frequencies fit the best with the orbital frequencies.

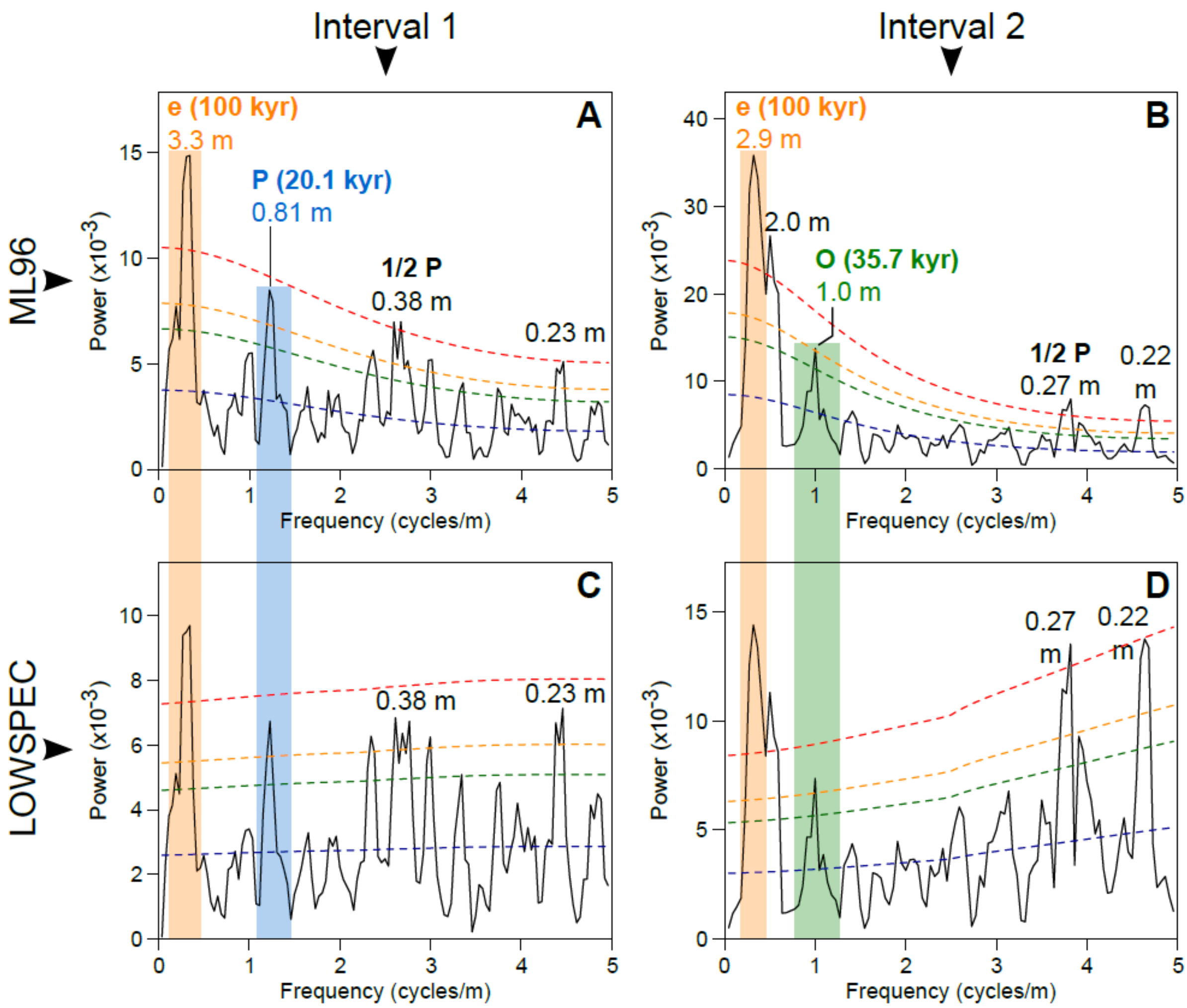


Fig. 6. 2π-MTM spectra of the magnetic susceptibility. **A. and B.** Spectra of intervals 1 and 2 with confidence levels calculated with the Mann and Lees (1996) method (ML96) with a Tukey's endpoint rule (Meyers, 2014). **C. and D.** Spectra of intervals 1 and 2 with confidence levels calculated with the LOWSPEC method (Meyers, 2012).

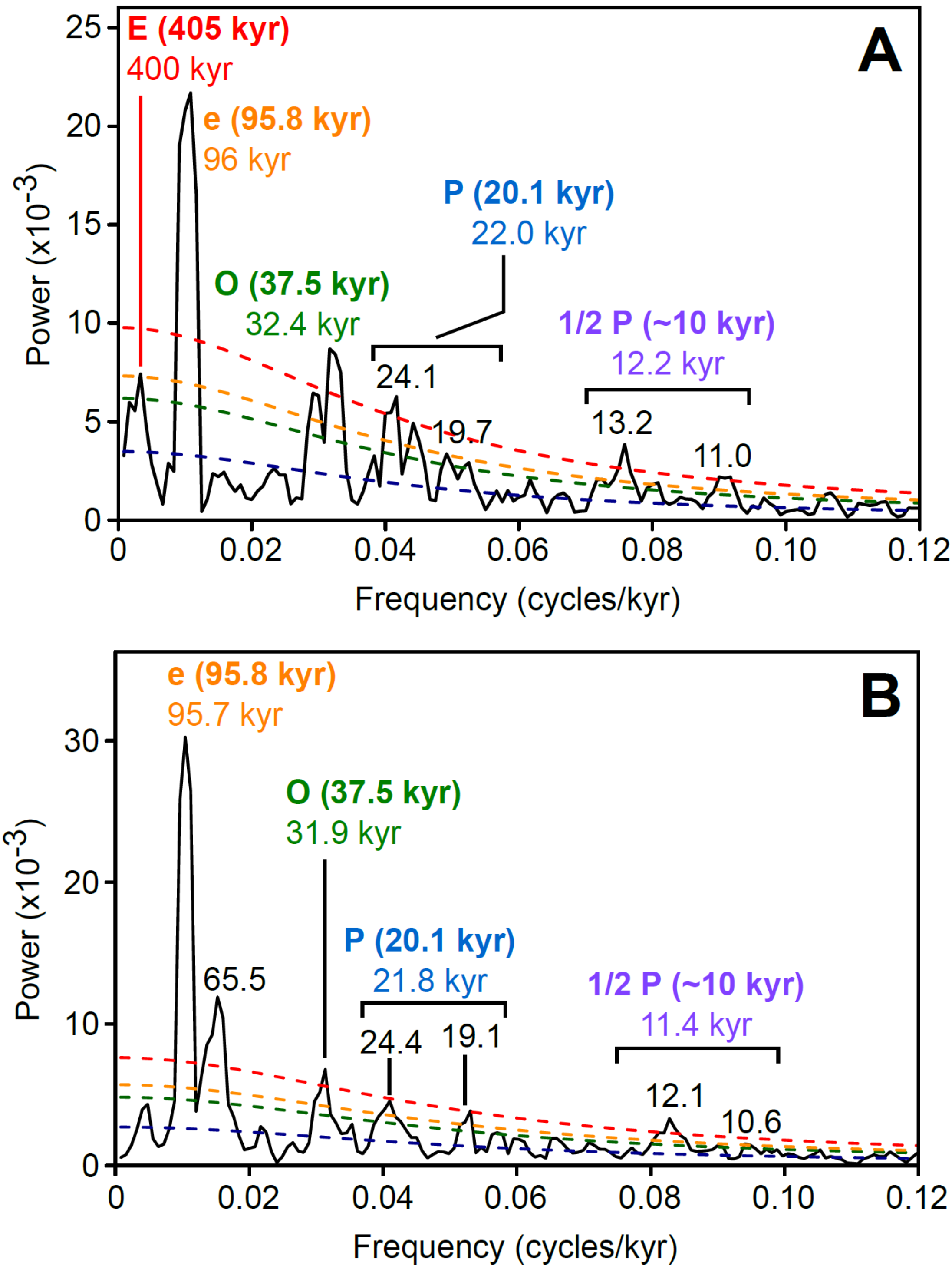
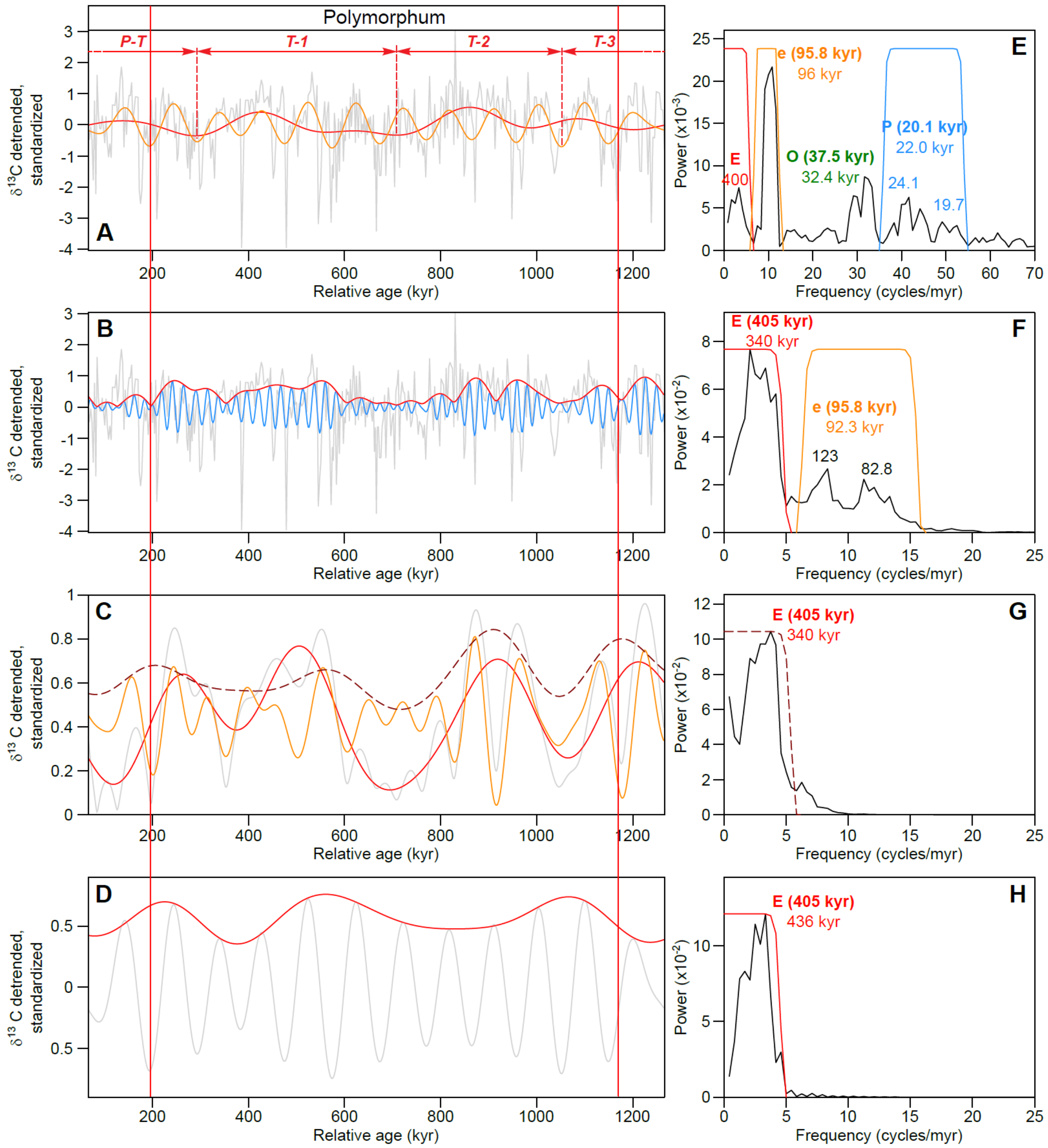


Fig. 7. 2π-MTM spectra of the (**A.**) calibrated $\delta^{13}C$ series, and (**B.**) calibrated MS series. The main periods are labeled in kyr. The theoretical period of the corresponding astronomical cycle is displayed in brackets. Abbreviations: E: 400-kyr eccentricity; e: 100-kyr eccentricity; O: obliquity.



Polymorphum
P-T
T-1
T-2
T-3
δ13C detrended, standardized
Relative age (kyr)
A
B
C
D
E
F
G
H
Power (x10-3)
Power (x10-2)
Frequency (cycles/myr)
e (95.8 kyr)
96 kyr
P (20.1 kyr)
22.0 kyr
O (37.5 kyr)
32.4 kyr
E
400
24.1
19.7
E (405 kyr)
340 kyr
e (95.8 kyr)
92.3 kyr
123
82.8
E (405 kyr)
340 kyr
E (405 kyr)
436 kyr

Fig. 8.

Fig. 8. Comparison between the direct filters of the eccentricity on the calibrated $\delta^{13}C$ signal and the amplitude modulation of the precession in the calibrated $\delta^{13}C$. **A.** Filter of the 405-kyr eccentricity (in red) and the 100-kyr eccentricity (in orange) of the calibrated $\delta^{13}C$ signal (in grey). **B.** Filter of the precession (in blue) and its amplitude modulation (in red) of the calibrate $\delta^{13}C$ signal (in grey). **C.** Filter of the 100-kyr cycle (in orange) and the 405-kyr cycle (in red) obtained from the amplitude modulation of the precession cycle (in grey). In dashed brown: Filter of the 405-kyr cycle obtained from the 100-kyr band of the amplitude modulation of the precession. **D.** Filter of the 405-kyr cycle obtained from the amplitude modulation of the direct filter of the 100-kyr cycle (in grey). **E.** Spectrum of the calibrated $\delta^{13}C$ series, with the filters used for the 405-kyr cycle (in red; frequency cut: 0.005833 cycles/kyr; roll-off rate: 10^{36}), the 100-kyr cycle (in orange; frequency cuts: 0.006667 – 0.01250 cycles/kyr; roll-off rate: 10^{36}) and the precession cycle (in blue; frequency cuts: 0.03583 – 0.05417 cycles/kyr; roll-off rate: 10^{36}). **F.** 2π-MTM spectrum of the amplitude modulation of the precession cycles. The red and orange curves represent the filter of the 405-kyr and 100-kyr eccentricity, respectively. The 405-kyr cycle is filtered with a Taner low-pass filter (frequency cut: 0.004833 cycles/kyr; roll-off rate: 10^{36}). The 100-kyr cycle is filtered with a Taner band-pass filter (frequency cuts: 0.006250 – 0.01558 cycles/kyr; roll-off rate: 10^{36}). **G.** 2π-MTM spectrum of the amplitude modulation of the 100-kyr cycle filtered from the amplitude modulation of the precession cycles. The 405-kyr cycle (in red) is filtered using a Taner low-pass filter (frequency cut: 0.005417 cycles/kyr; roll-off rate: 10^{36}). **H.** 2π-MTM spectrum of the amplitude modulation of the 100-kyr cycle filtered from the calibrated series. The 405-kyr cycle (in red) is filtered using a Taner low-pass filter (frequency cut: 0.004583 cycles/kyr; roll-off rate: 10^{36}). Note that spectra of panels F to H are obtained with a padding factor of 2.

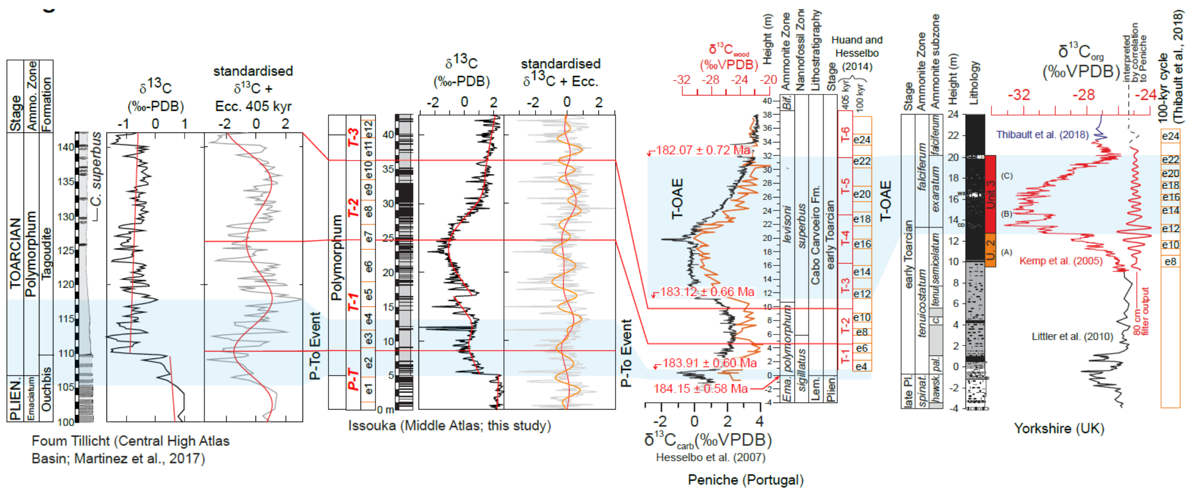


Fig. 9. Correlations of astronomical time scales in between the Central High Atlas Basin (Martinez et al., 2017), the Middle Atlas Basin (present study), the Peniche section (Suan et al., 2008b; Huang and Hesselbo, 2014) and the Yorkshire area (Thibault et al., 2018).