# Astronomical calibration of the Ocean Anoxic Event 1b and its implications for the cause of mid-Cretaceous events: a multiproxy record

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## Abstract

Cyclostratigraphic analyses were performed on magnetic susceptibility (MS), and elemental Ti and Fe series along the upper Aptian-lower Albian interval of the Poggio le Guaine (PLG) core, a Cretaceous pelagic succession in the Umbria-Marche Basin (central Italy). This interval represents one the most detailed and complete sedimentary archives and records oceanic perturbations associated with Oceanic Anoxic Event (OAE) 1b. The MS, Ti and Fe orbital control indicates a timespan of 2.68 Myr for OAE 1b event (114.10 to 111.34 Ma) and short eccentricity cycles played a key role, in controlling the amount of detrital input from weathering during monsoonal periods. Our chronostratigraphic study also provides age of 114.09 Ma for 113/Jacob, 113.25 Ma for Kilian, 112.67 Ma as a central age of the Monte Nerone cluster, 111.70 Ma for Urbino and 111.37 Ma for Leenhardt subevents, and a timespan of ~20 kyr for 113/Jacob, 70 kyr for Kilian, 670 kyr for Monte Nerone cluster, 60 kyr for Urbino and 60 kyr for Leenhardt levels. This study provides compelling evidence of the enormous potential C-isotope stratigraphy as tie points for cyclostratigraphic studies and as a valuable way to evaluate diachronism of bioevents. The organic-rich levels encompassing OAE 1b event has particular characteristics resulting from the combination of warm climate triggered by volcanic CO2 input, heavy precipitation, intense weathering and rapid marine transgressions, which leads the oceanic-atmospheric perturbations, acting as amplifiers of orbital forcings paleoclimate changes, resulting in deoxygenation and carbon burial during OAE 1b.

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# Astronomical calibration of the Ocean Anoxic Event 1b and its implications for the cause of mid-Cretaceous events: a multiproxy record

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**Key Points:**

- 405-kyr cycles in the magnetic suscepbility and XRF data indicate an astronomically paced deposition at PLG core during OAE 1b.
- High-resolution chronostratigraphic study provides a timespan of 2.68 Myr for the Oceanic Anoxic Event 1b.
- OAE 1b results from the combination of warm climate, heavy precipitation and intense weathering, acting as amplifiers of orbital forcings.

## Abstract

Cyclostratigraphic analyses were performed on magnetic susceptibility (MS), and elemental Ti and Fe series along the upper Aptian-lower Albian interval of the Poggio le Guaine (PLG) core, a Cretaceous pelagic succession in the Umbria-Marche Basin (central Italy). This interval represents one the most detailed and complete sedimentary archives and records oceanic perturbations associated with Oceanic Anoxic Event (OAE) 1b. The MS, Ti and Fe orbital control indicates a timespan of 2.68 Myr for OAE 1b event (114.10 to 111.34 Ma) and short eccentricity cycles played a key role, in controlling the amount of detrital input from weathering during monsoonal periods. Our chronostratigraphic study also provides age of 114.09 Ma for 113/Jacob, 113.25 Ma for Kilian, 112.67 Ma as a central age of the Monte Nerone cluster, 111.70 Ma for Urbino and 111.37 Ma for Leenhardt subevents, and a timespan of ~20 kyr for 113/Jacob, 70 kyr for Kilian, 670 kyr for Monte Nerone cluster, 60 kyr for Urbino and 60 kyr for Leenhardt levels. This study provides compelling evidence of the enormous potential C-isotope stratigraphy as tie points for cyclostratigraphic studies and as a valuable way to evaluate diachronism of bioevents. The organic-rich levels encompassing OAE 1b event has particular characteristics resulting from the combination of warm climate triggered by volcanic $CO_2$ input, heavy precipitation, intense weathering and rapid marine transgressions, which leads the oceanic-atmospheric perturbations, acting as amplifiers of orbital forcings paleoclimate changes, resulting in deoxygenation and carbon burial during OAE 1b.



## Plain Language Summary

The cause and effect of the Cretaceous Oceanic Anoxic Events (OAEs) are a motive of debate in the literature. One of the most important limitations to answer these questions is the age and duration of these events. The age uncertainty makes the correlations unreliable because the cause-effect is necessary to be time-dependent. In this work, we show the age and duration of the OAE 1b in different records and provide a correlation with orbital forcing and volcanic activity.

## 1 Introduction

The Cretaceous greenhouse climate system was punctuated by the occurrence of Oceanic Anoxic Events (OAEs) of regional to global expression (Schlanger & Jenkyns, 1976; Leckie et al., 2002; Herrle et al., 2004; Jenkyns, 2010), commonly characterized by enhanced marine productivity and oxygen deficiency that led to a great accumulation of organic matter at the seafloor and the deposition of black shale layers (Jenkyns, 2010).

The OAE 1b is a ca. 3 Myr long-lasting event (Leckie et al., 2002; Trabucho Alexandre et al., 2011; Coccioni et al., 2014; Sabatino et al., 2015, 2018) characterized by the occurrence of multiple subevents as prominent black shale layers in the Umbria Marche and Vocontian basins, namely 113/Jacob, Kilian, Urbino/Paquier, and, Leenhardt levels or equivalent (e.g., Coccioni et al., 2014; Kennedy et al., 2014; Bottini et al., 2015; Sabatino et al., 2015; Kennedy et al., 2017; Bottini and Erba, 2018; Matsumoto et al., 2020; Bodin et al., 2023). These layers are related to short-duration events of increased marine primary productivity and preservation of organic matter (Bodin et al., 2023) of continental origin (Sabatino et al., 2015) with occasionally e substantial marine contributions (Sabatino et al., 2015; Bodin et al., 2023).

The OAE 1b has been associated to global climate warming, with average sea surface temperature (STT) between 34°C and 36°C, and high ocean primary productivity (McAnena et al., 2013; Bottini et al., 2015; Bottini & Erba, 2018; Browning & Watkins, 2008; Sabatino et al., 2015), superimposed on influx of continental organic matter (Wang et al., 2022; Bodin et al., 2023). Such high productivity conditions may have been triggered by the emplacements of large igneous provinces (LIPs) such as the Southern Kerguelen (SK), Nauru-Mariana Plateau (NMP) and Ontong Java Plateau (OJP) (Eldholm & Coffin, 2000; Matsumoto et al., 2021, 2022; Davidson et al., 2023), modifying the paleoclimate and terminating the Cold Snap period (McAnena et al., 2013). Micronutrients originating during the emplacement of the LIPs might have fertilized the surface ocean and stimulated the marine primary productivity before and during the OAE 1b (e.g., Leckie et al., 2002; Browning & Watkins, 2008).

Unlike OAE 1a, characterized by a single condensed section deposited over ~1 Myr (Leandro et al., 2022), OAE 1b can be understood as a protracted long-lasting interval of organic carbon burial (Sabatino et al., 2015), with a cluster of several and extreme short-duration subevents (Grippo et al., 2004; Huang et al., 2010; Sabatino et al., 2015; Charbonier et al., 2023; Ait-Itto et al., 2023) and represents the longest perturbation of the global carbon cycle during the

Cretaceous period (Sabatino et al., 2015). The difference between OAE 1a and OAE 1b is also visible in the Osmium isotope, a suitable proxy for tracing hydrothermal activity, reveals marked differences between these two events (i.e., OAE 1a and OAE 1b). The former is characterized by a significant $^{187}Os/^{188}Os_i$ shift, while the second exhibits only some subevents that can be associated with volcanism and others with a possible monsoonal origin for some levels of OAE 1b (Matsumoto et al., 2022).

In the 1980s, OAE 1b was not individualized with a specific event, being described as part of the "Aptian-Albian OAE" (Schlanger & Jenkyns, 1976). Arthur et al. (1990) distinguished the Aptian/Albian anoxic events into OAE 1a and OAE 1b, proposing subevents or short-term organic carbon burial episodes associated with marine transgressions.  Herrle et al., (2004) constrained OAE 1b in the Aptian-Albian boundary, a section considerably restricted when compared to the definition by Coccioni et al. (2014) and the GTS2020. Some authors pointed out that Paquier Level is the sole representative of OAE 1b due to its exclusive 'paper-shale' characteristic and the heaviest $\varepsilon^{205}$ Tl anomaly as a proxy for globally significant ocean deoxygenation (Wang et al., 2022).

In this present work, the nomenclature used for OAE 1b follows Coccioni et al. (2014) for the Umbria-Marche Basin (UMB, central Italy) and Bodin et al. (2023) for the Vocontian Basin (France), where high concentrations of Hg (Sabatino et al., 2018), along with the continuously increasing trends of strontium and oxygen isotope not allow characterizing OAE 1b as a single event, but rather as a complex multiphase set of mostly negative $\delta^{13}C$ excursions spanning the Aptian/Albian interval containing widespread organic-rich layers. ).

The central–western Tethyan pelagic succession in the UMB holds complete and undisturbed records of the Aptian–Albian stages (Coccioni et al., 2012) including the lithological expression of the OAE 1b in the Marne a Fucoid Formation. The lithology of this formation consists of grayish-greenish, pelagic marls and marly limestones, alternating with black shales, but it is also characterized by some thick red-beds (e.g., Coccioni et al., 2012; Sabatino et al., 2015, 2018). These lithological alterations underline highly variable redox conditions at the bottom of the basin and suggest very unstable paleo-environmental and oceanographical conditions (Giorgioni et al., 2012, 2017). In this context, orbital perturbations were capable to change the palaeoceanographic regime by influencing the dispersal mechanism of the continental detrital input and nutrient supply (Tateo et al., 2000; Herrle et al., 2015; Wang et al., 2022).

Bodin et al. (2023) suggested that rhythmic changes in monsoonal activity, paced by Milankovitch cycles (long eccentricity), and their effect on the accumulation of organic matter in continental wetlands, explain the periodic shift in the global carbon isotope record throughout the OAE 1b interval.

Since the early 2000s, several studies have aimed to date the events that occurred during OAE 1b, detailing the aspect of "time," including both the time involved in the deposition of organic-rich levels and the time elapsed between these levels. Grippo et al. (2004) integrated earlier works with a time-series of photographic log of the Piobbico core (central Italy) and recognized a total of 29 long-eccentricity (405 kyr) cycles that resulted in an inferred duration of 11.8 ± 0.4 Myr of Albian. Huang et al. (2010), using high-resolution grayscale series of the pelagic Marne a Fucoidi again in the Piobbico core, covered the first third of OAE 1b and obtained a duration of 2.17 Myr between the Jacob and Kilian events, with a duration of 40 kyr and 120 kyr respectively.

Coccioni et al. (2014) estimated a timespan of 3.8 Myr for the entire OAE 1b (ages inferred after Grippo et al., 2004; Huang et al., 2010 and; Ogg and Hinnov, 2012). The latest Geologic Time Scale 2020 (Gale et al., 2020) documented a timespan of 1.3 Myr and 4.2 Myr between the Jacob to the Kilian and OAE 1b (Jacob to Leenhardt levels), respectively. Leandro et al. (2022) performed a cyclostratigraphic analysis based on high-resolution multiproxy ($\delta^{13}C$, $\delta^{18}O$, MS and ARM) dataset from the Poggio le Guaine (PLG) core and inferred a duration of 0.8 Myr between the Jacob and Kilian levels, with a duration of 30 kyr and 90 kyr, respectively. On the basis of magnetic susceptibility (MS) data and absolute dating from Selby et al. (2009), Charbonier et al. (2023) determined a duration of 25 kyr and 32 kyr for the Jacob and Kilian levels, respectively. Ait-Itto et al. (2023) using MS data of two sections of Col de Pré-Guittard (Vocontian Basin) determined a of 4.03 Myr for the interval encompassing the Jacob to Leenhardt levels. These results indicate that an ample duration between ~2.5 and 6 Myr of OAE 1b. However, a multiproxy characterization for this high-resolution interval associated with recent tie points from Herrle et al. (2015) and Bornemann et al. (2023)(after Selby et al., 2009), and the new biostratigraphic temporal calibration for the Aptian-Albian boundary by Leandro et al. (2022), suggest a duration of 3 Myr.

Significant efforts have been undertaken for correlating stable isotopes across different basins (Herrle et al., 2004; Coccioni et al., 2014; Bottini et al., 2015 Herrle et al., 2015; Fauth et al., 2022; Bornemann et al., 2023). Herrle et al. (2004), correlated various basins across different depositional environments ranging from terrestrial to hemipelagic settings. Herrle et al. (2015) correlated the carbonate carbon isotope composite age-calibrated curve (Ogg & Hinnov, 2012) with the geochemical records of Axel Heiberg Island, Nunavut (Canada) and expanded the identification of subevents to the North Atlantic. Fauth et al. (2022), through integration with biostratigraphy (planktonic foraminiferal and calcareous nannofossil bioevents) and carbon isotopes, conducted an astronomical calibration of a marine succession in the South Atlantic. Bodin et al. (2023) stated that the carbon isotope fluctuations across the OAE 1b cluster are the result of global disturbances in the carbon cycle that involved both atmospheric and oceanic systems, enabling the use of these fluctuations as universal tie points and suitable for cyclostratigraphic investigations.

This multidisciplinary study includes MS data, XRF (X-ray Fluorescence) measurements, stable isotope $\delta^{13}C$ correlations. In this paper, we apply cyclostratigraphic methodologies to identify the signal of orbital cycles in interval encompassing the OAE 1b of the PLG core (Coccioni et al., 2012; Savian et al., 2016; Matsumoto et al., 2021, 2022; Leandro et al., 2022), with the aim of inferring the time, duration, sedimentation rates, and evaluating the climatic forcing along the record. Furthermore, we correlate the PLG section with the other available carbon isotopes curves (Herrle et al., 2004, 2015; Fauth et al., 2022; Leandro et al., 2022; Charbonier et al., 2023; Bornemann et al., 2023) and estimate the ages of the various organic-rich sedimentary rocks associated to OAE 1b. The aim of this paper is also to integrate the recent findings (carbon isotopic fluctuations, new absolute ages, new cyclostratigraphic orbital tests) and generate a new chronostratigraphic interpretation in this interval to enhance the understanding of temporal variations during the OAE 1b event.

## 2 Materials and Methods

### 2.1 Poggio le Guaine Records: section and core

The Cretaceous pelagic succession of the UMB was deposited in a complex geological setting along the continental margin of the Apulian block, which was moving along with Africa towards northern Europe at that time (Channell et al., 1979). After decades of research, the Aptian–Albian pelagic succession of the UMB has become a classic reference record for regional to global scale paleoenvironmental studies on OAEs (Coccioni et al., 2014; Sabatino et al., 2015;

Savian et al., 2016; ; Sabatino et al., 2018; Leandro et al., 2022; Matsumoto et al., 2020, 2021, 2022). This succession was deposited well above the calcite compensation depth (CCD) at middle to lower bathyal depths (1000-1500 m) and at a paleolatitude of approximately 20ºN, on the south western margin of the Tethyan Ocean (Arthur & Premoli Silva, 1982; Coccioni et al., 1987, 1989, 1990, 1992; Savian et al., 2016).

The Aptian-Albian pelagic succession of the UMB extends from the upper part of the Maiolica Fm. (Tithonian to lower Aptian) to the lower part of the Scaglia Bianca Fm. (upper Albian to lower Turonian) and includes the Marne a Fucoid Fm. in between. The upper part of the Maiolica Fm. is represented by centimeter thick beds of white to gray limestone interspersed with black shales. The lower part of the Scaglia Bianca Fm. is characterized by centimeter thick beds of yellowish-gray limestones with reddish limestones and an interval with centimeter thick black shale layers in the lower part (Pialli level, Coccioni, 2001), which is part of the sedimentary expression of the lower part of OAE 1d.

The PLG section outcrops in the eastern portion of Monte Nerone (Figure 1; latitude 43º32'29.06" N, longitude 12º34'51.09" E). Lithologies comprises pale reddish brown to dark reddish brown and pale olive to greyish olive argillaceous limestones and calcareous marlstones, marlstones, slightly calcareous mudstones to argillaceous mudstones with several cyclically alternating organic–rich black shales and mudstones (Coccioni et al., 2014).

The drilling site of PLG core is located 400 m northwest of the PLG section (Coccioni et al., 2012) and has a straightforward correlation with it (Coccioni et al., 2014) so that geochemical, isotopic and micropaleontological data of outcrop and borehole core can be confidently integrated (Matsumoto et al., 2020).

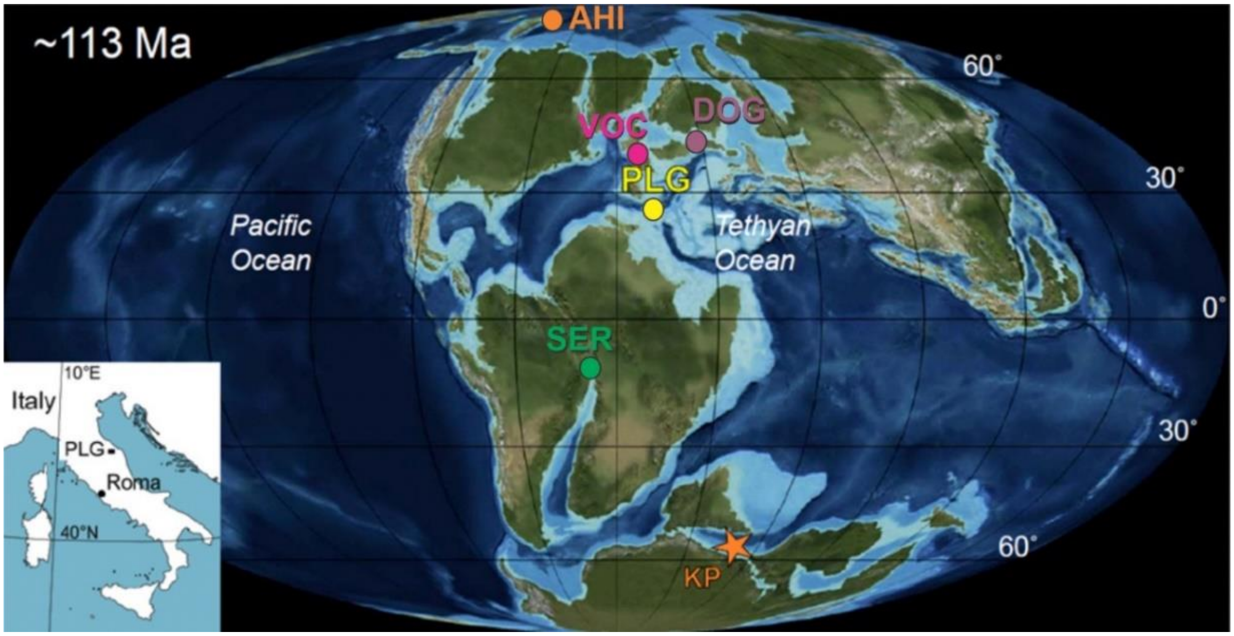



**Figure 1**. Paleogeographic reconstruction for the Aptian-Albian transition at ~113 Ma (modified after Sabatino et al., 2018) showing the location of the Poggio le Guaine (PLG), Vocontian Basin (VOC), Dolgen 3 core (DOG), Axel Heilberg Island (AHI), SER-03 core (SER) and of the Kerguelen Plateau (KP).

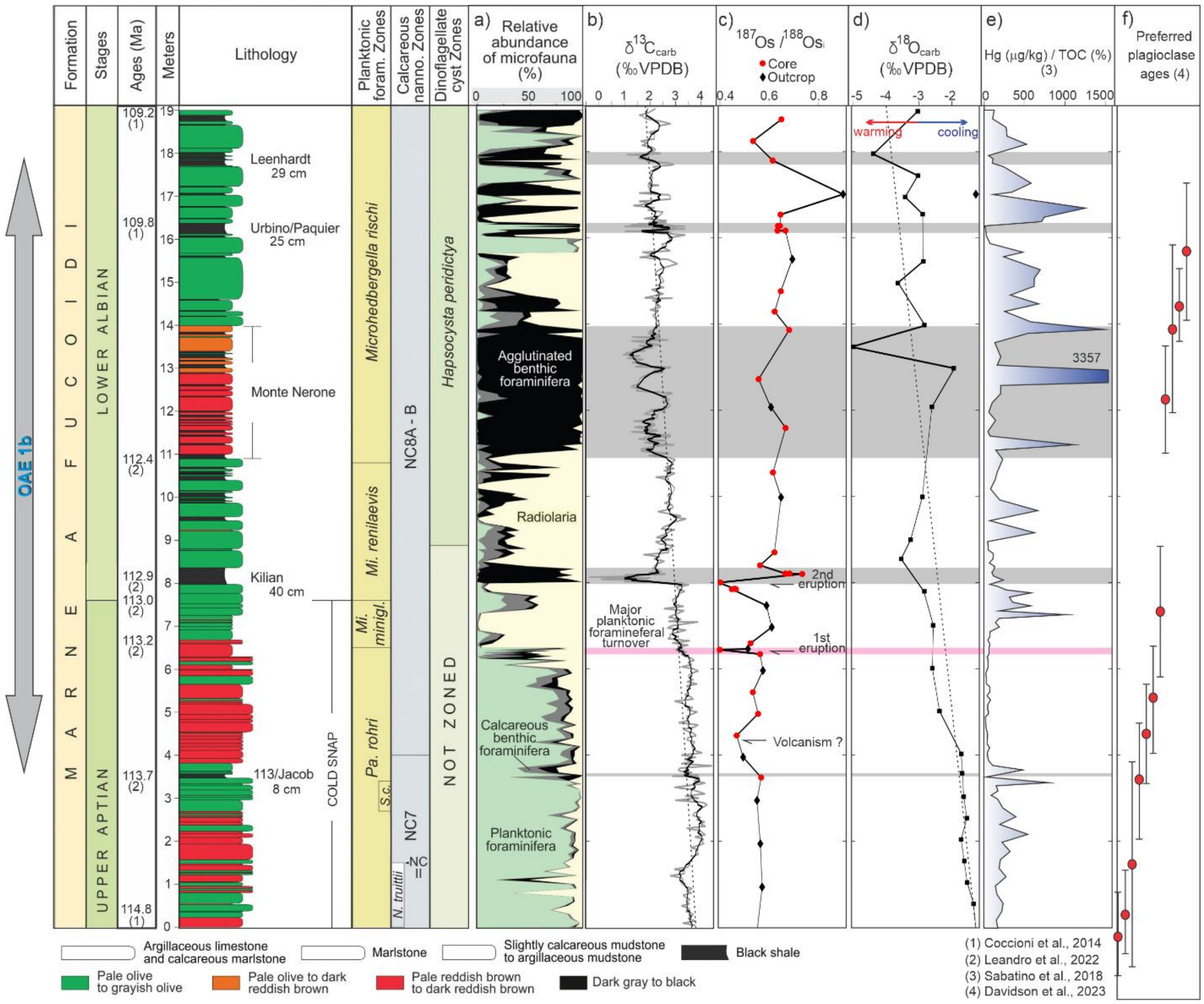
Several organic-rich horizons (Figure 2) representing the regional expression of the global OAE 1b have been identified (Coccioni et al., 1990, 2012; Coccioni, 1996; Leckie et al., 2002; Trabucho-Alexandre et al., 2011; Petrizzo et al., 2012; Coccioni et al., 2014; Sabatino et al., 2015, 2018; Matsumoto et al., 2020, 2022) and spanned from the upper Aptian to lower Albian (~114-109 Ma) (e.g., Coccioni et al., 2014). These events include the upper Aptian 113/Jacob, the lowermost Albian Kilian, the Albian Monte Nerone cluster, the Albian Urbino/Paquier, and the Albian Leenhardt levels (Coccioni et al., 2014; Sabatino et al., 2015, 2018; Matsumoto et al., 2020, 2022). According to the inferred ages of Leandro et al. (2022), the Aptian-Albian boundary is set at 113.0 Ma at PLG core in correspondence of the First Occurrence (FO) of *Microhedbergella renilaevis*, an age very similar to that attributed to Vöhrum's tuff (Selby et al., 2009).

High-resolution planktonic foraminiferal and calcareous nannofossil biostratigraphy, microfaunal (i.e., benthic and planktonic foraminifera, and radiolaria) assemblages, in combination with a detailed carbon and oxygen isotope record of the PLG section (Coccioni et al., 2014), associated with Os isotopic record (Matsumoto et al., 2020) and new preferred plagioclase ages (Davidson et al., 2023) were used to characterize OAE 1b in this work (Figure 2).

This integrated stratigraphic framework was correlated with PLG core data to build the base of our study. The lithological description of PLG section presented in Figure 2 (Coccioni et al., 2014) was transposed to PLG core to better illustrate lithological differences. The "red" layers named as CORBs (*Cretaceous Oceanic Red Beds*) (Wang et al., 2009) appear related with new preferred plagioclase ages from OJP volcanism (Davidson et al., 2023) and show an intrinsic relationship with changes in the relative abundance of microfauna (Coccioni et al., 2014) reflecting regional paleoenvironmental conditions.

The GSSP of Aptian/Albian boundary (i.e. the base of the Albian Stage) has been defined at Col de Pré-Guittard (Vocontian Basin, southeast France) and corresponds to FO of the planktonic foraminifer *Microhedbergella miniglobularis* within the thin organic rich Niveau Kilian level (Kennedy et al., 2017; Gale et al., 2020) coinciding with a negative carbon isotope excursion. The drop in the abundance of planktic foraminifera relative to benthic species that globally occur in deep-sea records (Huber & Leckie, 2011) is also shown at the PLG section across the Aptian/Albian boundary (Coccioni et al., 2014).

The abrupt planktonic foraminiferal turnover across the Aptian–Albian boundary during OAE 1b can be ascribed to enhanced ocean acidification caused by the massive release of volcanic $CO_2$ (Matsumoto et al., 2020). Abrupt Os isotopic shift to unradiogenic values and elevated Hg concentrations suggest multiple submarine volcanic events that correlate with new plagioclase ages, further increasing the relationship between the OJP and the paleoenvironmental changes during OAE 1b (Sabatino et al., 2018; Matsumoto et al., 2020; Davidson et al., 2023). The absence of physical evidence of unconformable surfaces (Coccioni et al., 2014), the deposition above CCD (Coccioni, 1990), the presence of the M0r reversal Chron as main tie point for the Aptian base (Savian et al., 2016) make the PLG a suitable reference record, ideal to test cyclostratigraphic techniques and dating major geological events (e.g., isotopes excursions, bioevents, volcanic pulses). Also, the clear orbital forcing response of several Tethyan records (Tateo et al., 2000; Grippo et al., 2004; Huang et al., 2010; Leandro et al., 2022; Charbonier et al., 2023) have stimulated this new cyclostratigraphic evaluation.




* a), b) Relative abundance of microfauna and carbon isotope records of Coccioni et al., 2014;c) $^{187}Os/^{188}Os_i$ records from Matsumoto et al., 2022; d) Oxygen isotope records from Leandro et al., 2022; e) Hg/TOC depth profiles from Sabatino et al., 2018; f) Prefered plagioclase ages and ranges from Davidson et al. ,2023

**Figure 2.** Stratigraphy of Aptian-Albian transition at Poggio le Guaine plotted against (a) the relative abundance of microfauna from Coccioni et al. (2014); (b) $\delta^{13}C_{carb}$ data from Coccioni et al. (2014); (c) $^{187}Os/^{188}Os$ isotopic record from Matsumoto et al. (2020); (d), $\delta^{18}O_{carb}$ data from Leandro et al. (2022); (e) Hg/TOC depth profiles from Sabatino et al. (2018); (f) preferred plagioclase ages from Davidson et al. (2023). The diamond and asterisk mark highest occurrence of *Pseudoplanomalina cheniourensis* and the lowest occurrence of *Pleurostomella subnodosa*, respectively. Key to planktonic and calcareous nannofossil abbreviations: *Pa.* = *Paraticinella*, *Mi.* = *Microhedbergella*, *minigl.* = *miniglobularis*, *S.* = *Shackoina*, *c.* = *cepedai*, *N.* = *Nannoconus.*

## 2.2 Sampling

The PLG core was drilled in 2010 and designed to provide a high-resolution reference record for the Aptian-Albian interval. Once in the laboratory, the core was split into two halves along the dip line of the bedding. The left side (archived) of the core was plastic coated, packed and housed at the University of Urbino (Italy). The right side (working half) of the core was cut into four parts, comprising two lateral sections, a bottom section, and the center of the split core (Savian et al., 2016). The center of the split core and bottom sections were cut in discrete cubic samples from the center of the split core sections in cubes of ~8 $cm^3$ for environmental magnetism analyses. Overall, we collected 3437 paleomagnetic samples with an averaging spacing of ca. 3 cm, from 0 to 95 meters along the PLG core. The weight of each sample was determined for subsequent mass normalization of magnetic properties. The same samples were also used for isotopic analyses. For this study, we only focused on OAE 1b interval from 1 to 19 meters resulting in 639 paleomagnetic samples with an averaging spacing of ca. 2.8 cm. The calcium carbonate ($CaCO_3$) content was compiled from Sabatino et al. (2015).

## 2.3 Magnetic susceptibility

The MS ($\chi$ mass specific normalized) measurements were carried out at the Paleomagnetic Laboratory of the University of São Paulo (USPMag, Brazil). Frequency dependence of the MS was measured in a total of 639 samples before remanence measurements. Measurements of the MS were made on an MFK1-FA Multi-Function Kappabridge (Pokorný et al., 2006) at three operating frequencies (976, 3904 and 15616 Hz) in a field of 200 A/m. For this work, we only used the 976 Hz frequency for the cyclostratigraphic study.

## 2.4 XRF measurements

The XRF data were collected using a S1 Titan handheld XRF spectrometer, with a slit of 1 cm parallel and 0.7 cm perpendicular to the core length, and a sampling rate of 5 cm. Analyses were made at the University of Urbino (Italy), conducted on the PLG core. A wide range of chemical elements was identified with two tube voltage settings: at 10 kV and 50 kV, each with five replicates and 30s acquisition time. After the measurement, anomalous values due to alteration of the core surfaces or analytical issues were removed from the series and the data were normalized respect to the total average of the series. Series of Ti and Fe were selected for cyclostratigraphic analysis and for paleoenvironmental interpretations. Approximately 561 data points were measured to construct the XRF-derived elemental time Ti and Fe series.

2.5 Stable carbon and oxygen isotopes

Carbon ($\delta^{13}$C) and oxygen ($\delta^{18}$O) stable isotopes analyses were performed in the carbonate fraction were performed at the University of Oxford (UK). A total of 465 bulk-rock samples were collected every ~5 cm and used to characterize the OEA 1b event. A rotary drill was used to obtain powder from the cubes used for magnetostratigraphic measurements. During sampling, veins containing diagenetic carbonate were avoided. A total of six triplicates and 28 duplicates of the same depth were used to evaluate the reproducibility of the isotopic data. The powders of 313 samples were analyzed using a VG Isogas Prism II mass spectrometer with an online VG Isocarb common acid-bath preparation system at University of Oxford (UK). All these samples were cleaned using acetone [$(CH_3)2CO$] and dried at 60 °C for at least 30 min. The powders of 33 samples were analyzed using a Kiel IV carbonate device coupled to Thermo Delta V Advantage mass spectrometer and nine samples were analyzed using a Gas Bench II carbonate device coupled to a Thermo Scientific Delta V mass spectrometer. Samples were reacted with purified phosphoric acid ($H_3PO_4$) at 70–90°C in all instruments. The calibration was undertaken using the Oxford in-house Carrara marble standard (NOCZ) and NBS-19 (TS-Limestone). Data are reported relative to the Vienna Pee Dee Belemnite (VPDB) scale. The reproducibility of replicated standards (1σ) was < 0.09‰ for $\delta^{13}$C and < 0.10‰ for $\delta^{18}$O. The maximum difference between triplicate and duplicate samples from the same depth were 0.31‰ for $\delta^{13}$C and 0.39 ‰ for $\delta^{18}$O.

2.6 Cyclostratigraphic Analysis

Cyclostratigraphic analyses on MS and XRF-derived Ti and Fe records were realized by using *Acycle* software (Li et al., 2019) version 2.4.1. Regarding the MS dataset exhibited a non-stationary variance, it has been log-transformed for variance stabilization. Such pattern was not observed for the Fe and Ti datasets and hence it was not necessary to conduct the log-transformation. All series were then linearly interpolated every 2 cm, which is the mean spacing of the Fe, Ti and MS series. Prior to the spectral analysis, all datasets were detrended by using the “loess” method with a running window of 35% of the data lengths.

Spectral analysis was conducted by the prolate multitaper spectral estimator (MTM, Thomson, 1982) associated with the robust first-order autoregressive red-noise modeling (Mann & Lees, 1996). The persistence and/or transience of the astronomical signals along the series were assessed by means of Evolutive Harmonic Analysis (EHA) (Meyers et al., 2001). Regarding the best identification of the low-frequency spectral content at the MS-based analysis, we chose to solely discuss the results on the sediment average rate (SAR) (Meyers, 2015, 2019; Li et al., 2018) provided from the MS series. For this, we conducted a time-scale optimization analysis (*TimeOpt;* Meyers, 2015) in order to recover the optimal sedimentation rates and to evaluate the sedimentation accumulation rate (SAR) changes in MS data. Such results were further compared with the correlation coefficient (COCO) and evolutionary COCO (eCOCO) analyses (Li et al., 2018).

Potential astronomical frequencies that may correspond to those expected for the Tethyan pelagic succession in the UMB at Aptian–Albian times (Huang et al., 2010; Grippo et al., 2014; Leandro et al., 2022) were chosen based on the La2004 astronomical solution (Laskar et al., 2004). To convert MS and $\delta^{13}C_{arb}$ data from depth to time domain and, hence, to build an age model for the studied stratigraphic interval of the PLG core, we performed the astronomical tuning for MS series by means of a dynamically filtering (available at the *Acycle* package) that allows us to isolate the interpreted long-eccentricity component sinusoidal curve from the datasets tuned according to the La2004 $g_2$-$g_5$ target curve.

We used the $^{206}Pb/^{238}U$ absolute age of the basal Albian for the Schwicheldt Ton Member, Gault Formation, Vöhrum, Germany (Selby et al., 2009; Bornemann et al., 2023) and U-Pb age (111.74 ± 0.26 Ma, using bentonite zircons) dating of the Invincible Point Member of the Christopher Formation (Herrle et al., 2015) as tiepoints for astronomical tuning, and compare with the ages of Jacob and Kilian levels (Leandro et al., 2022). This tie point approach is quite different from previous cyclostratigraphic works for Aptian-Albian intervals as it overcomes the problem of diachronism between bioevents and enables correlation between basins.

## 3 Results

### 3.1 XRF

After normalization by mean and operation of dividing by the standard deviation, Ti normalized values vary from -2.4 to 5 and Fe from -2 to 3, and their variations could be used as proxies of detrital supply (Herbert et al., 1986) and continental runoff (Arz et al., 1998). A more distinct linear trend is observed in the Ti series compared to the Fe series; however, both datasets exhibit a fairly similar pattern. It is possible to observe oscillations in the Ti and Fe profiles with wavelengths of approximately 0.5 meters, modulated (superimposed) by cycles with 2 meters, Figure 3. Cycles with great periods are also present, and some minima for these cycles coincide with boundary of important intervals, like the Monte Nerone cluster (Figure 3b and 3c). Prominent cycles with meter scale wavelengths (~0.5-0.7 m) coincide with the major planktonic foraminiferal turnover and intervals with main paleoceanographic significance such as the Kilian and Leenhardt levels, and some black shale levels in the Monte Nerone cluster (Figure 3b and 3c), suggesting that these features are somehow controlled by cyclical variations of this order of magnitude.

### 3.2 Magnetic Susceptibility

The MS underlies the amount of magnetic minerals (e.g., Liu et al., 2020) and could also be used as a proxy for detrital input throughout Fe minerals. Our MS record (mean of $\chi = 7.7 \times 10^{-8}$ $m^3$/kg) exhibited three stratigraphic long-term quasiperiodicies (~ 6 m) that would be partly associated with microfaunal changes (Figure 3d). The 1.0-3.5 m basal interval is characterized by the lowest values of MS that might be ascribed to low sedimentary input, which is followed by a 5-m-thick interval marked by the highest values MS and reddish lithologies between 113/Jacob and below Kilian levels.

The Monte Nerone cluster (11.0 m – 14.0 m; Coccioni et al., 2014) is marked by relatively stable MS values. Such lithostratigraphic interval is also characterized by a cyclic pair of black shales and mudstones with the dominance of agglutinated foraminifera. The upper part of the studied interval is quite different from the lower one. Short oscillations (~ 0.5 m wavelengths) were noticed, which resemble a similar pattern observed at the microfaunal variations and $CaCO_3$ content (Figure 3d and 3e). The Urbino/Paquier black shale (16.0 m – 16.4 m; Figure 3d) corresponds to a prominent negative short-term variation of MS.

### 3.3 $CaCO_3$ content

The percentages of $CaCO_3$, a proxy of surface carbonate productivity, ranges from 3 to 78 wt% (Figure 3e). The lowermost stratigraphic portion (1-11 m) exhibits a long-lasting decreasing trend interrupted by short-term variations (from a few centimeters to a few meters) coinciding with intervals enriched in organic matter. Noteworthy, two coexisting bundling patterns (~ 0.5 m and ~ 1.0 m, respectively) are clearly observed, both displaying amplitude oscillations of approximately 20 wt%. Above the Monte Nerone cluster, the $CaCO_3$ values increase with respect to the lower interval. In general, low values of $CaCO_3$ are recorded in the black shale levels. A sharp decrease (from ~ 60 to ~30 wt%) was noticed at the same position of a foraminiferal turnover (Coccioni et al., 2014). Just above the OEA 1b onset, there is a three-meter interval (from 3.5 to 6.5 m) with higher $CaCO_3$ values (greater than 60 wt%.), which coincides to a higher MS value interval. Such interval, where apparently both MS and $CaCO_3$ contents evolve in phase (highlighted in blue, Figure 3e) is also coincident with the abnormally high Mn/Al ratio (Sabatino et al., 2015).

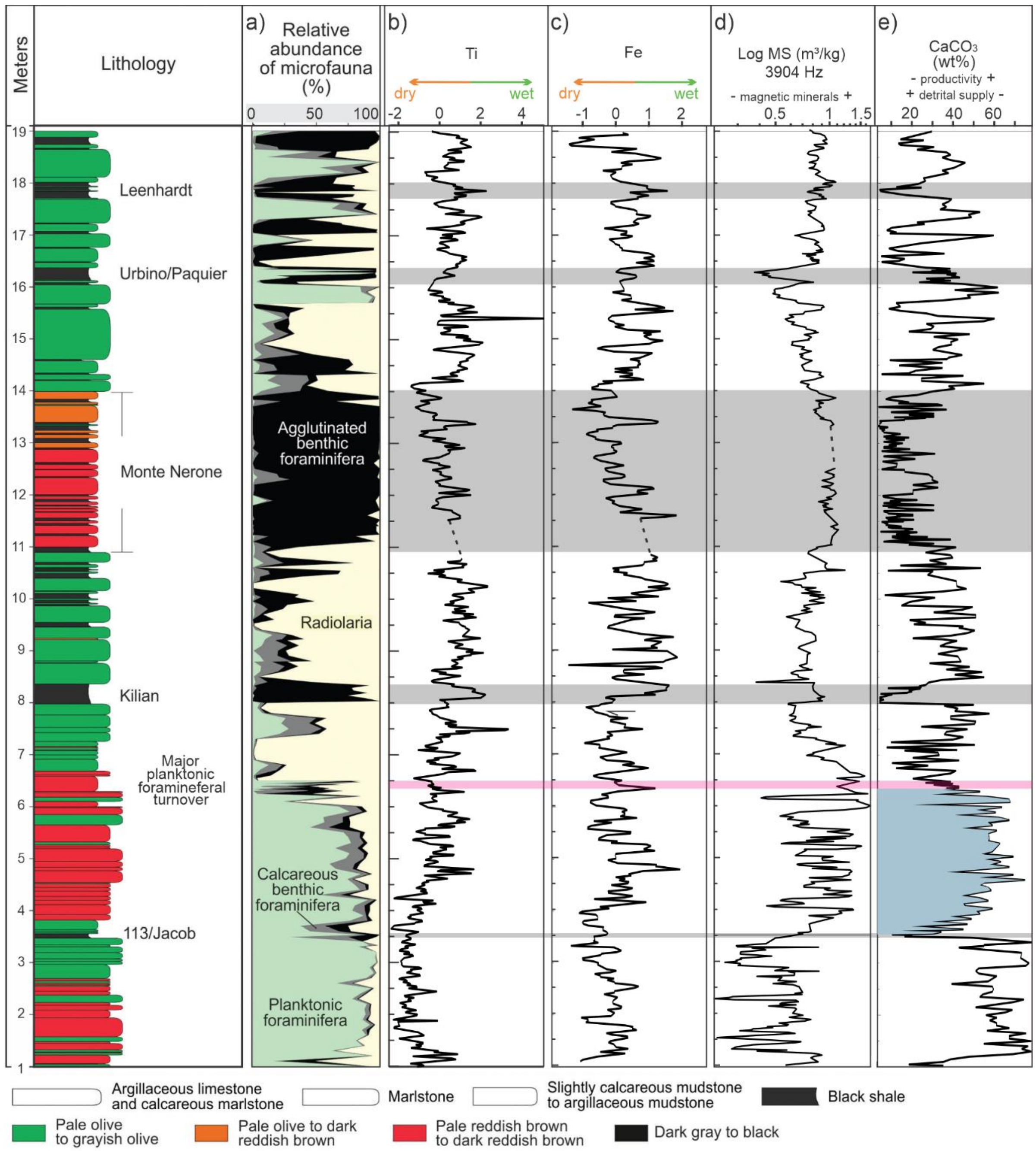



**Figure 3.** Lithology of the Poggio le Guaine section (Coccioni et al., 2014) plotted against the paleoclimatic proxies: (a) Foraminiferal and radiolarian abundance from Coccioni et al. (2014); (b) Ti content; (c) Fe content; (d) MS; (e) $CaCO_3$ from Coccioni et al. (2014). Pale blue represents a distinct interval where both MS and $CaCO_3$ present high values and are not in opposite phase.

### 3.4 Cyclostratigraphy

A number of studies (e.g., Huang et al., 2010; Grippo et al., 2014; Leandro et al., 2022) reported that Cretaceous sedimentary processes occurring along the pelagic Marne a Fucoidi Fm. in the UMB were controlled by orbitally induced climatic changes. In this work, the studied interval partially overlaps with the upper record of PLG core studied by Leandro et al. (2022), and we intend to verify whether the 405-kyr-based ATS inferred by this study could be extended upwards, hence reaching the OAE 1b interval.

Two long eccentricity cycles are expected between the Jacob and Kilian levels (comprising a timespan of ~ 810 kiloyears). Thus, the 405 kyr cycle should have an approximate wavelength of ~ 230 cm (~0.4 cycles/m). A spectral analysis was performed on the OAE 1b segment to identify the presence of these specific cycles and the others cycles at Milankovitch bands (Figure 4b and 4c). We compared the results obtained from various detrends before applying the LOESS detrend, elevating confidence levels of long and short eccentricity cycles. Despite the recognition of a visual record suggests the presence of a linear trend in the MS data, the comparison between the original spectrum harmonized by applying the logarithm and the same data after linear detrending (Figure supplementary S1) reveals that linear detrending before LOESS was unnecessary.

MTM-based spectral analyses of the Log MS datasets before and after detrending process (Figure 4d, e) exhibited a range of frequencies with significant spectral peaks exceeding the 90% confidence level (CL), with some peaks exceeding the 99% CL. After characterize values from 0.35 to 0.55 cycles/m as the spectral band of the long-eccentricity cycle (405 kyr) we could verify that low frequency spectral peaks (left portion of Figures 4e and 4f, highlighted by green bands) are associated with million-year scale band (MSB), and the two next peaks besides 405 kyr (right portion of Figures 4e,f, highlighted by blue bands) are associated with 125 kyr and 95 kyr short-eccentricity cycles, respectively, and the width of highlighted rectangles corresponding to Milankovitch period uncertainties (Waltham, 2015).

The same process could also be applied for estimating other cycles, predicted in the astronomical solution La2004 (Laskar et al., 2004), in Milankovitch band and defining the associated frequencies and wavelengths. Patterns revealed by combining the MTM and EHA analyses indicated that the spectral peaks (Log MS) with 243 cm, 71 cm and 55 cm could represent the expression of the 405-kyr, 125-kyr and 95-kyr eccentricity cycles (Figure 4e, f).

Other peaks ranging from 45-32 cm could be associated with secondary short eccentricity periods (Laskar, 2020). A careful analysis of LOESS trends reveals a combination of longer cycles (e.g., 1600, 1000 and 700 kyr) also suggesting a interesting link between MSB and CORBs intervals (red beds), not addressed in this study.

At the stratigraphic depth of ~ 13 m, there is a small interval (~ 40 cm) with a lack of magnetic susceptibility data (Figure 4), hindering the detection of cycles with wavelengths at the end of the short eccentricity. In order to test the feasibility of "interpolating" this interval, we conducted a comparison between Lomb-Scargle (Schulz and Stattegger, 1997) and MTM (Thomson, 1982) power spectra. The Lomb-Scargle power spectrum allows to perform the analysis of unevenly spaced time series, which are usually irregularly spaced in time and can be processed directly (Schulz and Stattegger, 1997). Despite the expected compromise in detecting high frequencies, the 405 kyr signal is present with the same characteristic band, enabling the continuation of the cyclostratigraphic analysis process (Figure S2).

The interpolation sampling rate could be a sensitive point of discussion. The XRF-derived series were acquired at 5 cm resolution rate, while the MS series at 2.8 cm. Since these rates exceed the interpolation performed in the cyclostratigraphic analyses (2 cm), it might raise questions, particularly when indicating the preservation of the precession signal along the PLG core. As we can see in Figure 5, the higher-frequency precession cycle has a wavelength of about 11 cm, and the overall resampling of all proxies to 2 cm does not impact the recognize of the Milankovitch cycles.

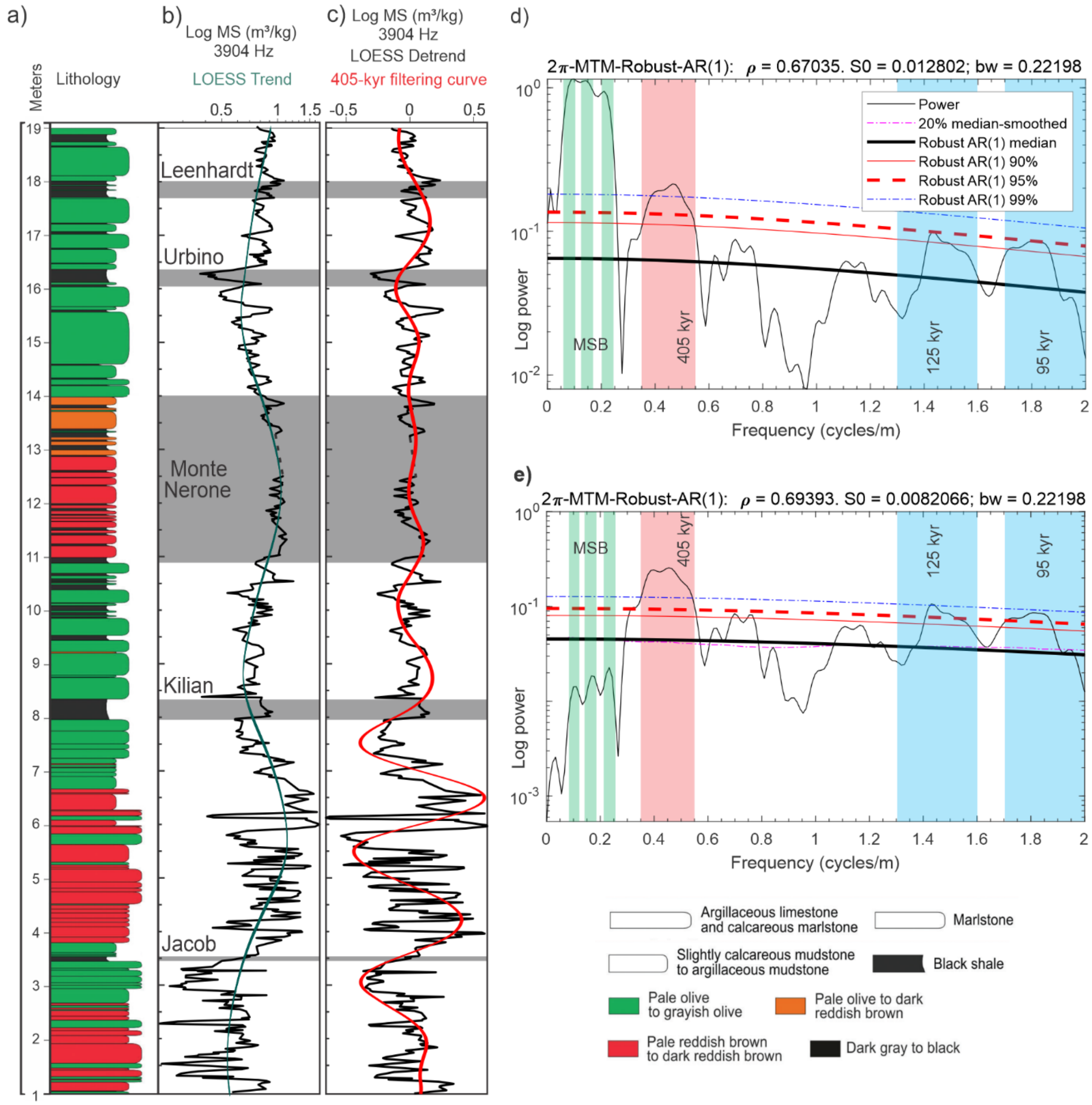
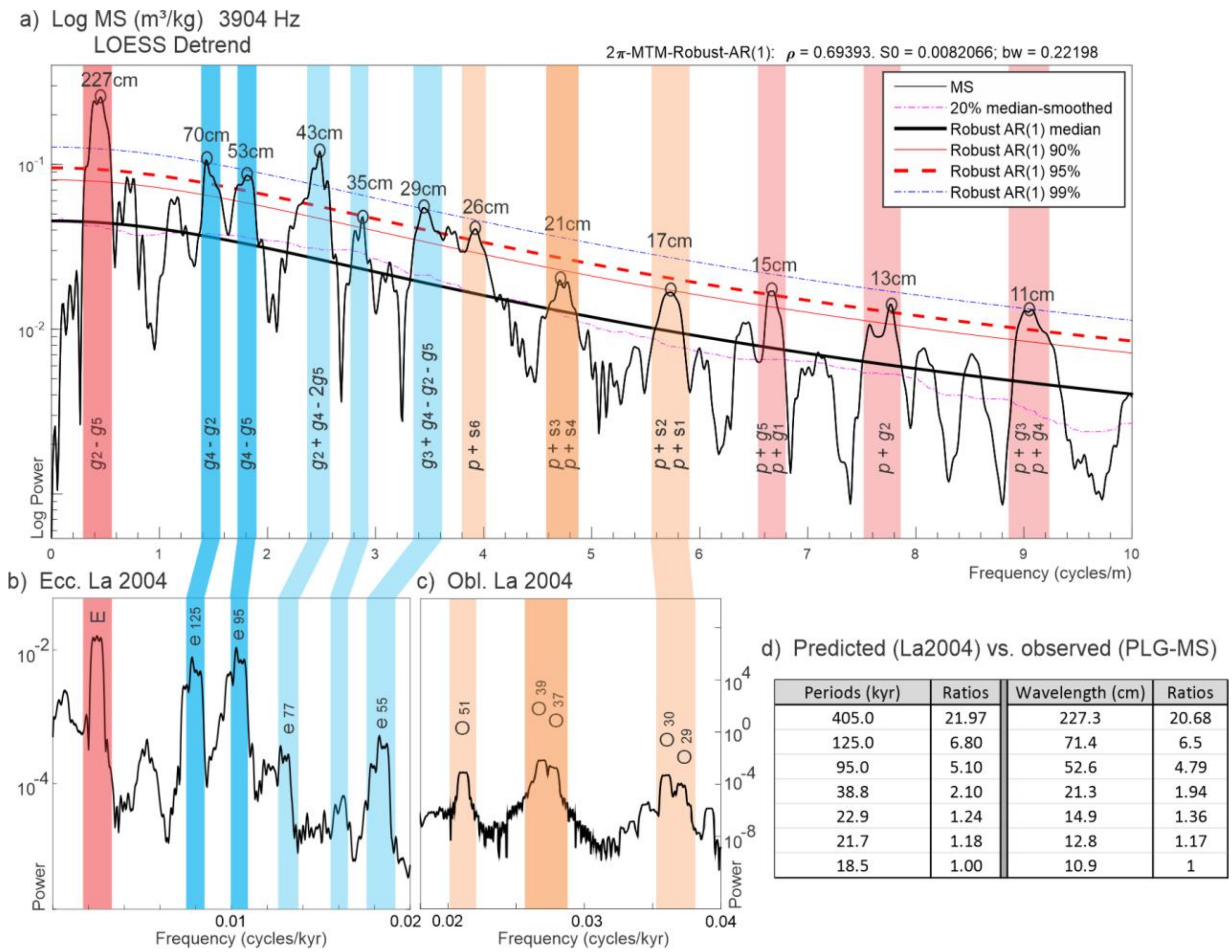



**Figure 4.** Detrend analysis for Log magnetic susceptibility (MS) depth-domain data for the PLG core: a) Lithology of the PLG section (Coccioni et al., 2014) transposed to PLG core. Grey bands represent the OAE 1b sub-events; b) Log MS (black line) record together with LOESS trend (green line) showing the inferred relationship between long-period cycles and CORBs intervals; c) LOESS detrend curve of Log MS data series (black line) together with 405 kyr filtered signal (red line); d) 2π MTM power spectrum associated with the first-order autoregressive (AR1) confidence levels showing the normal high power of Myr cycles compared to others cycles peaks. e) 2π MTM power spectrum associated with the first-order autoregressive (AR1) confidence levels after LOESS detrend. The colors at power spectrums are: pale green = MSB (million-year scale band); pale red = $E_{405}$; light blue = short eccentricity.

Comparing the power spectrum of MS (Figure 5a) with the predicted eccentricity and obliquity spectra (Figure 5c and 5d) in the astronomical solution by Laskar et al. (2004), it is possible to identify and correlate the major peaks within theoretical solutions. Assigning the median value of 0.44 cycles/m as the average frequency of the long-eccentricity cycle (wavelength 227.3 cm) we verified for specific spectral peaks in the Log MS ~ (227.3:71.4:52.6:21.3:14.9:12.8:10.9 = 20.7:6.5:4.8:1.9:1.4:1.2:1), resembling the predicted Milankovitch spectral peak ratios for Albian times (405:125:95:38.8:22.9:21.7:18.5=22:6.8:5.1:2.1:1.24:1.18:1) (Waltham, 2015) (Figure 5d).

The four eccentricity signals (cycles of 131, 125, 99, and 95 kyr), formed by the most powerful short eccentricity astronomical signals of La2004 (Laskar et al., 2004) and, simplified here as a pair composed of the e125 kyr ($g_4$ - $g_2$) and e95 kyr ($g_4$ - $g_5$) signals, are clearly visible next to the long eccentricity signal of 405 kyr. Additionally, we can observe the eccentricity peaks of e77 kyr ($g_2$ + $g_4$ - $2g_5$) and e55 kyr ($g_3$ + $g_4$ - $g_2$ - $g_5$), although the former exhibits an excessively high-power value. The same outcome can be seen in Leandro et al. (2022), where the e77 kyr and e55 kyr frequency bands were described as transient periodicities. The frequency band of the e55 kyr signal (Figure 5b, light blue band), the short eccentricity signal with the highest frequency among the corresponding cycles (Laskar, 2020), appears to be nearly superimposed on the 51 kyr obliquity band ($p$ + $s_6$), due the proximity of their frequencies. This proximity leads to a noteworthy increase in the power associated with the e55 kyr signal. In the La2004 solution, the obliquity signals related to the pair O39 kyr ($p$ + $s_3$) and O37 kyr ($p$ + $s_4$) exhibit the highest power when compared to the O51 kyr signal (Laskar, 2020). However, probably due to the simultaneous occurrence of this signal and the e55 kyr signal, there is an amplification in the power values. The pair of peaks related to the obliquity signals of O30 kyr and O29 kyr are also visible and correlational between the predicted and observed spectra (Figure 5a and 5c).




| Periods (kyr) | Ratios | Wavelength (cm) | Ratios |
|---|---|---|---|
| 405.0 | 21.97 | 227.3 | 20.68 |
| 125.0 | 6.80 | 71.4 | 6.5 |
| 95.0 | 5.10 | 52.6 | 4.79 |
| 38.8 | 2.10 | 21.3 | 1.94 |
| 22.9 | 1.24 | 14.9 | 1.36 |
| 21.7 | 1.18 | 12.8 | 1.17 |
| 18.5 | 1.00 | 10.9 | 1 |

**Figure 5.** Comparison between the power spectrum of magnetic susceptibility (MS) from the PLG core and the spectrum predicted in the astronomical solution La2004 (Laskar et al., 2004): a) Logarithmic MS displaying combinations of secular frequencies. The values of the respective cycle wavelengths (in centimeters) were extracted at the locations indicated by the black circles; b) La2004 astronomical solution (Eccentricity) for ages between 110 and 115 Ma; c) La2004 astronomical solution (Obliquity) for ages between 110 and 115 Ma; d) Comparison between the predicted (La2004) and observed (Log MS of PLG core) ratios for Albian times. The colors at power spectrums are: pale red = $E_{405}$; light blue = short eccentricity; Orange = Obliquity peaks (dark-orange, mean obliquity cycle); Pale Pink = Precession index peaks. More details about combinations of secular and fundamental frequencies described here are available at Laskar (2020).

After the analysis of MS data and the definition of the specific bands for each cycle, we performed a joint analysis of MS, Ti and Fe. LOESS detrend and MTM-based spectral analyses of the Ti, Fe and Log MS datasets exhibited a range of frequencies with significant spectral peaks exceeding the 95% CL (Figure 6a, 6b and 6c), with some peaks exceeding the 99% CL. The wavelength ratios verified for specific spectral peaks in the Ti ~

(217.4:66.7:55.6:20.4:14.3:12.2:10.9 = 20:6.13:5.1:1.9:1.3:1.12:1) and Fe ~ (219.8:66.7:55.6:22.7:15.1:13.9:10.9 = 20.2:6.13:5.1:2.1:1.4:1.05:1) spectra well correspond to the predicted Milankovitch spectral peak ratios for Albian times (405:125:95:38.8:22.9:21.7:18.5= 22:6.8:5.1:2.1:1.24:1.18:1) (Waltham, 2015). The combination of the MTM and EHA analyses suggested that the spectral peak bands with 260–210 cm, 70 cm and 60–54 cm wavelengths could be the expression of the 405-kyr, 125-kyr and 95-kyr eccentricity cycles, respectively. Other peaks ranging from 45-32 cm could be associated with secondary short eccentricity periods (Laskar, 2020).

Although we clearly identified an unequivocal record for the long and short-eccentricity cycles in Ti, Fe and MS data sets, it is also possible to recognize obliquity and precession cycles. The precessional cycle is present in the spectra with amplitudes near 99% CL revealing that the median sample rate of series is enough to preserve all Milankovitch cycles described in La2004 solution (Laskar et al., 2004).

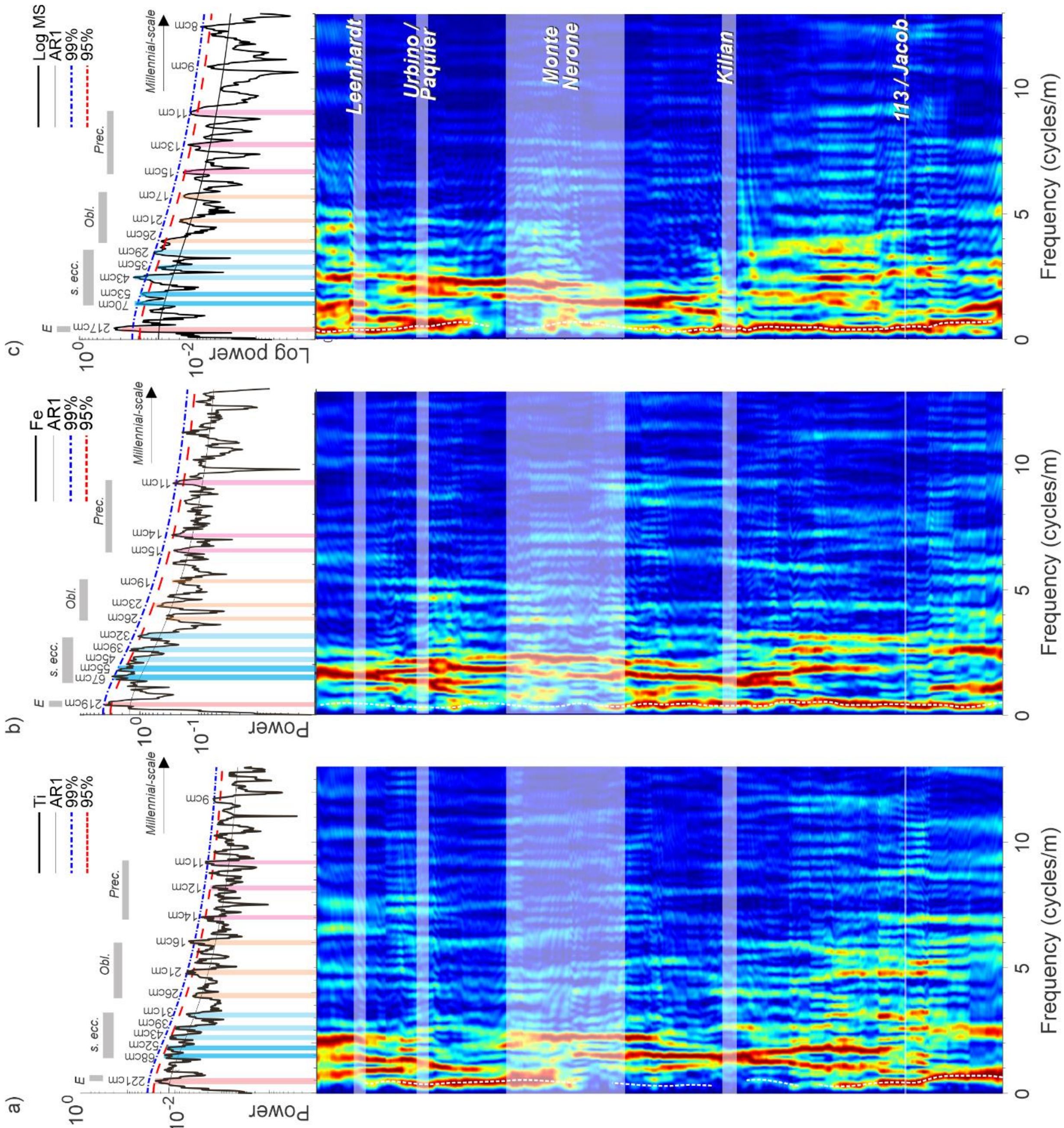



**Figure 6.** Cyclostratigraphic analyses for the LOESS detrended: a) Ti ; b) Fe and c) Log MS depth-domain data sets for PLG core. Top - 2π multi-taper method (MTM) power spectrum associated with the first-order autoregressive (AR1) confidence levels. Bottom - normalized amplitude of an evolutive harmonic analysis (EHA). The dashed line indicates the tracking wavelength record of the long-eccentricity ($E_{405}$) component for the datasets; d) The color bands in power spectrums represents $E_{405}$ – (pale red), short eccentricity (light blue); obliquity (orange), and precession index (light pink). White shaded areas represent major organic matter-rich levels of OAE 1b.

### 3.5 Phase relationship of Log MS data and Laskar's astronomical solutions

Before astronomical tuning process, we performed an evaluation of Log MS 405 kyr filtered signal phase in relation to different Laskar's astronomical solutions (Laskar et al., 2004, 2011a, 2011b) (Figure 7). Vöhrum's tuff stratigraphic level is closely located above the carbon isotope negative excursion of the Kilian level at Dolgen 3 core (Borneman et al., 2023) with an age of 113.1 ± 0.3 Ma (Selby et al., 2009). The correlation between the 405 kyr signal extracted from the MS curve and the approximate positioning of the tuff in relation to the Kilian level indicates that the tuff is located near a peak (maximum) of long eccentricity. Based on the error range of the absolute age from Selby et al. (2009), we can infer that the point of maximum eccentricity in the cycle labeled with the letter "B" is the best candidate as a tie point.

Thus, 112.8 Ma is the minimal age (youngest) for the Vöhrum's tuff and the Kilian level (little older) must be placed in the same long eccentricity cycle (Figure 7a). We do not know the equivalent level of the Vöhrum's tuff in UMB, but carbon isotope correlations and the FO of *Prediscosphaera columnata* constrain it within the *M. renilaevis* planktonic foraminiferal zone, totally within a unique long eccentricity cycle (named here B, Figure 7a). As we can observe, the age range related to the Vöhrum's tuff is likely in phase with the long eccentricity cycle named 'B,' and the negative excursion related to the Kilian Level in the $\delta^{13}C$ curve is located in the decreasing portion of cycle 'B' towards the initial minimum of eccentricity in cycle 'A' (Figure 7c, yellow band). So, assuming the tuff's age is correct, it is unlikely that the negative excursion of the Kilian level is correlatable with cycle 'A,' which has an approximate age of 113.6 Ma (as suggested by Fauth et al., 2022).

Phases analysis of 405 kyr long eccentricity of Laskar's solutions indicate that between 113 and 113.2 Ma the maximum peaks of all Laskar's astronomical solutions are present and we can associate the maximum of "B" Log MS filtered 405 cycles with any point in this interval (Figure 7c). The maximum of "B" Log MS filtered 405 cycle (Figure 7a) is stratigraphically above Kilian Level that is positioned at the PLG core in ascendent portion (between the beginning of B cycle, or fist minimum, and the maximum of B) of the same cycle. So, it is expected that the Kilian level must occur between 113.10 Ma (La2010b) – 113.24 (La2004) Ma. It is worth mentioning that this age range does not invalidate or support other ages of Kilian outside the Tethyan realm (Fauth et al., 2022; Leandro et al., 2022). The discussion of synchronism of anoxic events around the world is not the objective of this work. We evaluated two possibilities of phase relationship (direct=cave-cave and opposite=cave-peak) and concluded that, similar to Leandro et al. (2022), the direct way (cave-cave) is more plausible and double-check both tie points. High eccentricity values mean a high influx of terrigenous material and, consequently, higher Fe minerals concentration that increases MS values.

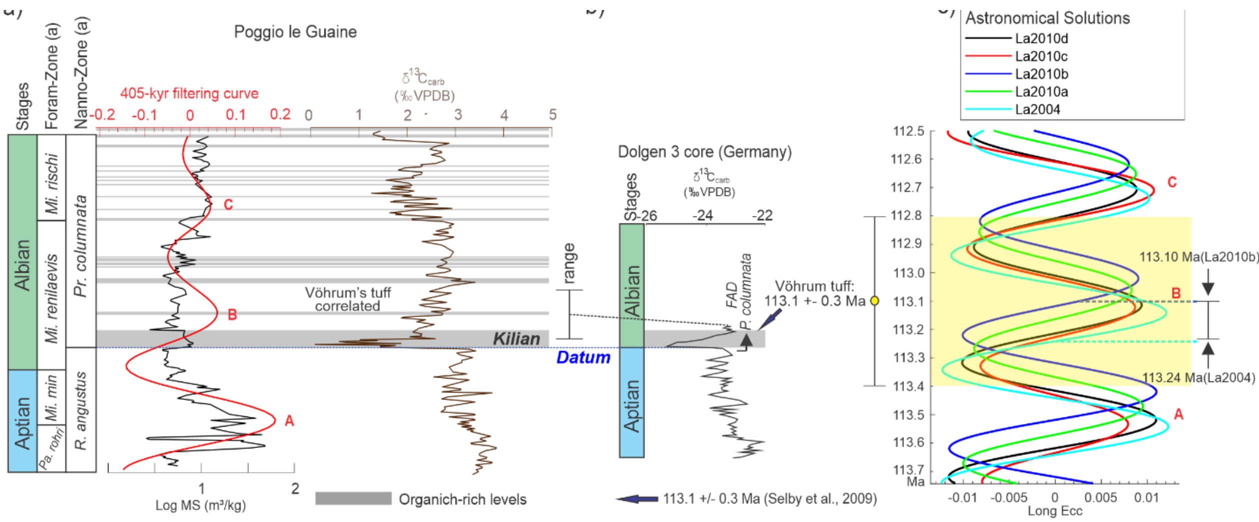



**Figure 7.** Evaluation of Log MS 405 kyr filtered signal phase of the Kilian Level based at different Laskar's astronomical solutions (Laskar et al., 2004, 2011a, 2011b): a) The Kilian Level at PLG core together with biozones (Coccioni et al., 2014) and 405 kyr Log MS filtered signal; b) Tentative of transpose Vöhrum's tuff stratigraphic position between Dolgen 3 core (Borneman et al., 2023) and PLG core; c) Phases of 405 kyr long eccentricity of Laskar's solutions indicate that age range of 113.0-133.2 Ma coinciding with the near maxima eccentricity of all solutions of a cycle named as B.

### 3.6 Tiepoints transposing process based on $\delta^{13}C$ chemostratigraphy

Since there are no available radiometric ages for the Aptian-Albian interval of the PLG core, it was necessary to transpose tiepoints between different places though correlations based on stable $\delta^{13}C$ chemostratigraphy. Even in distinct geological contexts (different depositional environments), the shapes of the $\delta^{13}C$ curves could be correlated to each other (Bodin et al., 2023) and use them as global tiepoints. These correlations aim to reconcile the $\delta^{13}C$ markers with numerical ages. We correlate carbon isotope stages (CIS) (Herrle et al., 2004; Coccioni et al., 2014; Leandro et al., 2022) and highlight prominent features, represented by excursions, peaks, troughs, and breaks in the long-term behavior of the carbon isotope curves, using the sequence of letters from the Greek alphabet, from **α** to **ο**, where: ***k*** is the onset of the Killian excursion and F.O. of *M. renilaevis*; **λ** is the Kilian prominent negative carbon excursion; **μ** is the end of this excursion, coincident the Vöhrum tuff horizon (Bornemann et al., 2023), and the **o** marker (positioned by correlation in ~17 m, at PLG) is stratigraphically placed very close to absolute U-Pb 111.74 ± 0.26 Ma age estimation (bentonite zircons) from Herrle et al. (2015) (Table 1 and Figure 8).

We also used stages definitions, foraminiferal and nannofossil events (Herrle et al., 2004, 2015; Coccioni et al., 2014; Leandro et al., 2022; Fauth et al., 2022; Bornemann et al., 2023) to correlate CIS intervals, and match Glendonite beds (Herrle et al., 2015) as an effect of Cold Snap interval to reinforce our age's transposition. The ammonite zones, even with the possibility of occurrence in a limited region (Kennedy et al., 2014), have also been included in our correlation's framework. We used transposed ages as anchors at the beginning of tuning process, and later it was released during direct correlation between 405 kyr Log MS filtered signal.

**Table 1:** Major features associated with C-markers.

Table 1 Characteristics and positioning of c-markers into chemostratigraphic stages in PLG.

| C-marker | CIS | F.Z. | N.Z. | Characteristics |
|---|---|---|---|---|
| α | Ap 6-7 | *L. cabri* | NC 6 | Higher $\delta^{13}C$ peak at the base of a high values plateau in the *L. cabri* foraminiferal zone. |
| β | Ap 7 | *L. cabri* | NC 7 | Lower $\delta^{13}C$ peak within a high values plateau in the in *L. cabri* foraminiferal zone. |
| γ | Ap 7 | *G. ferr* | NC 7 | Higher $\delta^{13}C$ peak at end of a high values plateau in the *G. ferr.* foraminiferal zone. |
| δ | Ap 8 | *G. alger* | NC 7 | Lower $\delta^{13}C$ shift above a high values plateau at the base of the *G. alger.* foraminiferal zone. |
| ε | Ap 11-12 | *H. troc* | NC 7 | End of a low $\delta^{13}C$ values plateau and beggining o increasing trend in the *H. trocoidea* foraminiferal zone |
| ζ | Ap 12 | *H. troc* | NC 7 | End of a $\delta^{13}C$ increasing trend in the *H. trocoidea* foraminiferal zone |
| η | Ap 13 | *P.rohri* | NC 7 | Relatively higher $\delta^{13}C$ peak within a high values plateau across the *H. troc./Pa. rohri* foraminiferal zones. |
| θ | Ap 15 | *P.rohri* | NC 7 | Higher $\delta^{13}C$ peak at the top of a high values plateau in the *Pa. rohri* foraminiferal zone. |
| ι | Ap 15 - Al1 | *Mi.min* | NC 8A-B | Lower $\delta^{13}C$ peak at the top of a decreasing trend in the *Mi. min.* foraminiferal zone. |
| κ | Al1 | *Mi.ren* | NC 8A-B | Abrupt higher $\delta^{13}C$ peakin the *Mi. ren.* foraminiferal zone, preceding the Kilian negative excursion. |
| λ | Al1 | *Mi.ren* | NC 8A-B | Abrupt lower $\delta^{13}C$ peak in the *Mi. ren.* foraminiferal zone, associated with the Kilian event. |
| μ | Al1 | *Mi.ren* | NC 8A-B | Positive $\delta^{13}C$ shift in the *Mi. ren.* foraminiferal zone, above the Kilian negative peak. |
| υ | Al1 | *Mi.rischi* | NC 8A-B | Top of a $\delta^{13}C$ decreasing trend in the *Mi. rischi* foraminiferal zone. |
| ξ | Al 2-3 | *Mi.rischi* | NC 8A-B | Top of a $\delta^{13}C$ increasing trend in the *Mi. rischi / planispira* foraminiferal zone, near the Paquier event. |
| ο | Al 3-4 | *Mi.rischi* | NC 8A-B | Abrupt break on $\delta^{13}C$ increasing trend in the *Mi. rischi / planispira* foraminiferal zone, Urbino event. |

The Aptian OAE 1a C-isotope excursion was explained by the emplacement of massive OJP LIP (Bralower et al.,1999; Tedeschi et al., 2017). In the Tethys, the *Selli Level* (Coccioni et al., 2014) and *Goguel Level* (Charbonier et al., 2023) or simply OAE 1a (Herrle et al., 2015, Gale et al., 2020) events are black shales associated with this volcanism. However, new $^{40}Ar/^{39}Ar$ data suggest that the eruptive history of the OJP was much younger (Davidson et al., 2023), enabling an important link between the peaks of volcanism during OAE 1b (Matsumoto et al., 2022) and OJP eruptions.

The top of OAE 1a event is characterized by a positive excursion name here by **α** (Figure 8) expressed as a higher $\delta^{13}C$ peak at the base of a high values plateau in the *L. cabri* foraminiferal zone. Positive long-term C-isotope trend is interrupted by a negative excursion (lower peak) detectable mainly in the Tethyan realm, associated with *Niveau Blanc* (Herrle et al., 2004; Charbonier et al., 2023) and *Wezel* (Matsumoto et al., 2020; Leandro et al., 2022), pointed as **β**. Leandro et al. (2022) dated this anoxic episode at 117.9 Ma. The upper part of the positive interval described as Ap 7 C-isotope stage (Herrle et al., 2004; Leandro et al., 2022) is followed by a huge negative excursion that coincides with *G. ferreolensis*/*G. algerianus* biostratigraphic zones boundary. The most $\delta^{13}C$ positive peak in *G. ferreolensis* at the end of high values plateau was named **γ**, a higher peak at end of a high values plateau.

The **δ** marker is clearly visible around all regions of Earth, associated with *NCC2* (Herrle et al., 2004; Charbonier et al., 2023) and *Noir* (Charbonier et al., 2023, Gale et al., 2020), also recognized by the long-term inflection change in the carbon isotope curve ,as a lower $\delta^{13}C$ shift above a high values plateau at the base of the *G. algerianus* foraminiferal zone. Except for the (relatively small) negative excursion associated with the Fallot level or FA 3, from this point onward, the curves show a gradual decrease in $\delta^{13}C$ values until the **ε** marker, where a significant shift in curve behavior occurs, and values begin to increase. These markers end a low $\delta^{13}C$ values plateau and begins an increasing trend in the *H. trocoidea* foraminiferal zone.

The **ε** marker is related to the onset of a C-isotope positive shift, which marks the beginning of a long interval with relatively high $\delta^{13}C$ values, in which the **ζ**, **η** and **θ** markers could be defined. This interval is related to a cooler period called *Cold Snap* in the Tethyan Ocean (McAnena et al., 2013; Bottini et al., 2015; Leandro et al., 2022; Bodin et al., 2023). The **ζ** marker is characterized as the end of a $\delta^{13}C$ increasing trend in the *H. trocoidea* foraminiferal zone, while the **η** marker is a relatively higher $\delta^{13}C$ peak within a high values plateau across the *H. trocoidea* / *Pa. rohri* foraminiferal zones.

Herrle et al. (2015) positioned the Jacob Level at Axel Heiberg below the position where the long-term trend of carbon isotope curve inflects, named as **η** marker. This feature is related to Ap 13 C-isotope stage in the Vocontian Basin, but Charbonier et al. (2023) dated the Jacob Level as a 114 Ma, within the Ap 15 C-isotope stage. Leandro et al. (2022) dated the Jacob event at 113.7 Ma that is characterized as a $\delta^{13}C$ negative excursion (Figure 8c).

The **θ** marker is the highest $\delta^{13}C$ peak at the top of a high values plateau in the *Pa. rohri* foraminiferal zone. Above this marker, the C-isotope curves slightly decrease and are punctuated by a short-term and high amplitude oscillation, marking the Kilian sub-event in the Tethyan realm (Bréhéret, 1983, 1988). The next interval is characterized by a decreasing trend representing Ap12-14, of which the lowest values are associated with the onset of OAE 1b event. Within the following decreasing trend, a rapid fluctuation occurs in the correspondence of the Kilian Level, a standout feature near the Aptian-Albian boundary (Herrle et al., 2004, 2015; Coccioni et al., 2014; Leandro et al., 2022; Fauth et al., 2022; Bornemann et al., 2023). The Kilian Level, labelled here as **λ** marker, is one of the most prominent features at the Aptian-Albian interval and an important marker for approximating the Aptian-Albian boundary (Petrizzo et al., 2012; Coccioni et al., 2014; Charbonier et al., 2023). It is characterized by a $\delta^{13}C$ positive excursion followed by a negative excursion in the Tethyan realm (Vocontian Basin and UMB).

The **μ** marker is a positive $\delta^{13}C$ shift in the *Mi. renilaevis* foraminiferal zone, above the Kilian negative peak. This level is associated with an age of 113 Ma (Gale et al., 2020; Leandro et al., 2022). The Vöhrum's tuff was identified above the Killian's excursion (Bornemann et al., 2023). The Kilian Level (top of Ap 15 C-stratigraphy stage or FO of *M. renilaevis*) shows a very minor positive excursion in the Atlantic Ocean (Axel Heiberg Island, North Atlantic Ocean and SER-0, South Atlantic Ocean) (Figure 8a and 8d). The Cedar Mountain Formation (USA) $\delta^{13}C$ curve also reveals a similar pattern (Ludvigson et al., 2010; Fauth et al., 2022).

Herrle et al. (2015) positioned the Kilian Level quite distant from the Albian base, with a U-Pb absolute age of 111.74 ± 0.26 Ma, using bentonite zircons for an interval remarkably close to the Kilian Level. In our correlation, this age corresponds to an interval close to **ξ** marker. Therefore, the signature that Herrle et al. (2015) attributed to the Kilian Level, is here correlated to the Paquier (**ξ** marker) or Urbino Level (Coccioni et al., 2015; Charbonier et al., 2023). Consequently, the interval attributed to the OAE 1b at Axel Heiberg Island (Herrle et al., 2015) is here related to the Leenhardt Level (Coccioni et al., 2015; Charbonier et al., 2023), and represented as a **ο** marker.

The **ξ** marker represents a negative peak associated with the Paquier Level in the Vocontian Basin (Herrle et al., 2004), and a ~0.4‰ fluctuation corresponding to the Urbino

Level in the PLG record (Coccioni et al., 2014). Above, in the Al3-5 interval, the $\delta^{13}C$ curve reaches a minimum and then increases.

Below the **ν** marker, oscillations occur within the Monte Nerone interval at PLG without significant expressions in the isotopic curve in the Vocontian Basin, despite correlations between Monte Nerone and levels HN 3-HN 7 (Herrle et al., 2004; Coccioni et al., 2014). The Invincible Point Member of the Christopher Formation was dated at 111.74 Ma using bentonite zircons and falls close the **ο** marker in the Axel Heilberg Island section (Herrle et al., 2015). The exact stratigraphic positioning of this dating is difficult to correlate with PLG and Vocontian sections, and thus, this was used solely as an age control point for the upper boundary of the studied section in the tuning process.

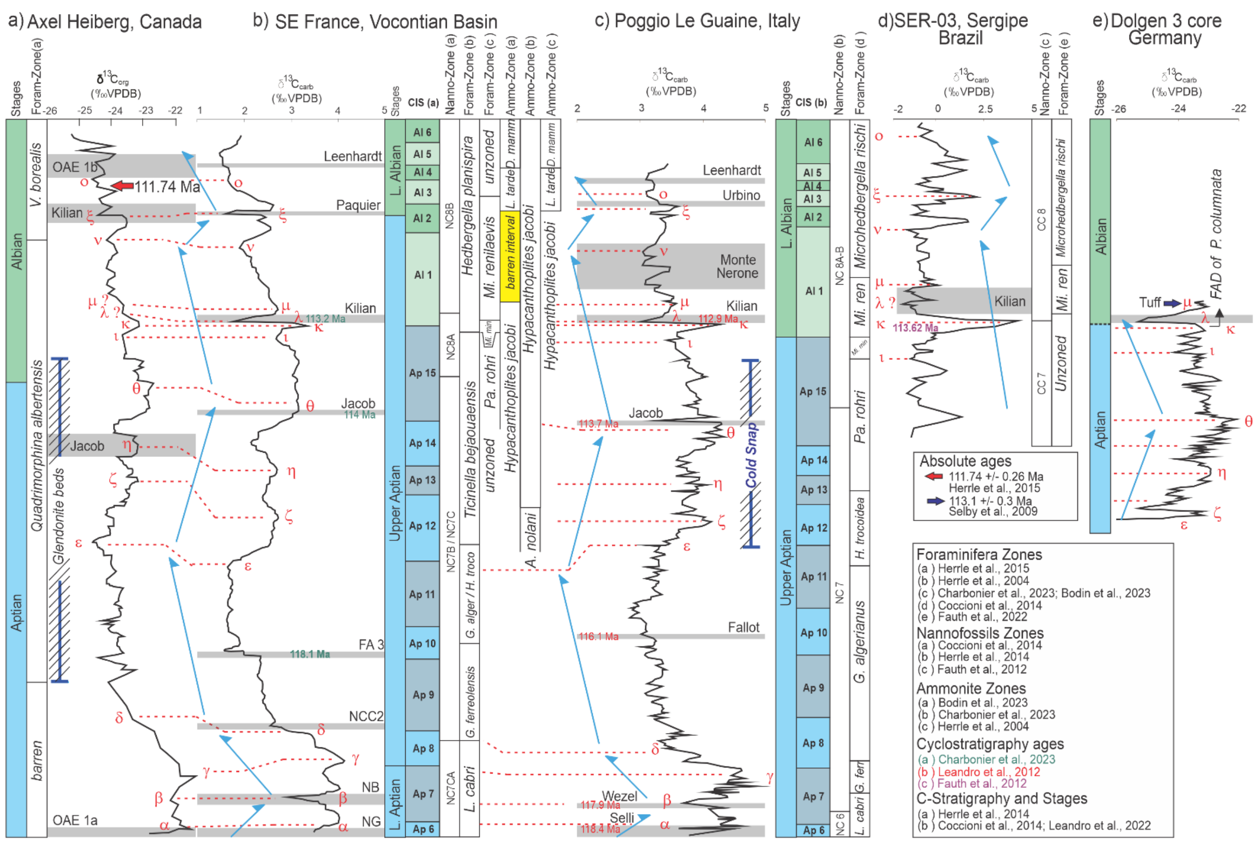



**Figure 8.** Correlation of C-isotope records showing the major patterns and C-marks of: a) Axel Heiberg Island, Canada; b) Vocontian Basin, France; c) PLG core, Italy; d) SER-03, Sergipe Basin, Brazil; e) Dolgen-3 core, Germany. Absolute ages and biozones are detailed in the legend. Grey shadings represent OAE 1b sub-events. Modified from Fauth et al. (2022), Leandro et al. (2022), Herrle et al. (2015),

Coccioni et al. (2014), Herrle et al. (2010), Boudin et al. (2023), Charbonier et al. (2023), Nebe (1999) and Bornemann et al. (2023). Blue arrows indicate the long-term trends.

3.7 Astronomical tuning

Astronomical tuned Log MS data (Figure 9) were constructed after long-eccentricity component interpretation in MS dataset with the La2004 astronomical solution (Laskar et al., 2004). Figure 9a shows lithological changes along the PLG section (Coccioni et al., 2014) alongside the cyclostratigraphically estimated ages determined in this study. Figure 9b provides LOESS detrended Log MS dataset and 405 kyr dynamically filtered signal used for tuning, anchored in CIS transposed absolute ages highlighted with red (111.74 ± 0.26 Ma, Herrle et al., 2015) and blue arrows (113.1 ± 0.3 Ma, Selby et al., 2009) and the stratigraphic position of C-isotope stages (Greek letters, in red). Using a dynamic filter with cut-off frequencies between 0.35 and 0.55 cycles/m, we isolated the interpreted 405-kyr long-eccentricity component within the MS dataset. Then, we constructed the ~405-kyr tuned age model for the PLG utilizing the output of this long-eccentricity filter (Figure 9b, red line) and aligning it with the $g_2$-$g_5$ target curve from the La2004 astronomical solution (Figure 9d, red line) for the Aptian-Albian interval (Laskar et al., 2004). This resulted in an average sedimentation rate of 0.5 cm/kyr (Figure 9c). The sedimentation rate undergoes an increase from 0.42 to 0.65 cm/kyr until reaching the Monte Nerone Level, after which it decreases to 0.47 cm/kyr, indicating a paleoenvironmental change identifiable through a notable variation in sediment coloration.

This procedure allowed us to build a FATS based on a sequence of 9 long-eccentricity cycles (E3 to E-5, written in red, where E0 is related to Kilian Level) and an age model for the studied interval in the PLG core spanning ~3.4 Myr (19–1 m) (Figure 9e). For OAE 1b event (i.e. from the base of Jacob Level to the top of Leenhardt Level) a timespan of ~2.76 Myr is obtained. From the MS data age model, we can infer ages of ~113.55 Ma and ~113.33 for FO and LO (last occurrence) *M. miniglobularis*, ~113.33 and ~112.82 Ma for FO and LO of *M. renilaevis*, ~112.82, the latter coincides with FO *Microhedbergella rischi*. Also, we can infer ages of major black shale levels in the PLG core. After tuning, we checked ages and timespan of all geological features (e.g., biozones, black shales, CORBs) along the study interval and estimated ages for C-marks. The ~1-m-thick bundles are associated with 405 kyr half-cycles, while oscillations of around ~0.5 m exhibiting significant amplitudes are correlated with short eccentricity cycles. These are modulated by longer cycles, contributing to a sedimentation rate ranging from ~0.4 to 0.8 cm/kyr. High frequency cycles (11-26 cm) created by obliquity and precession orbital modes are also present, where the latter is modulated by short eccentricity cycles.

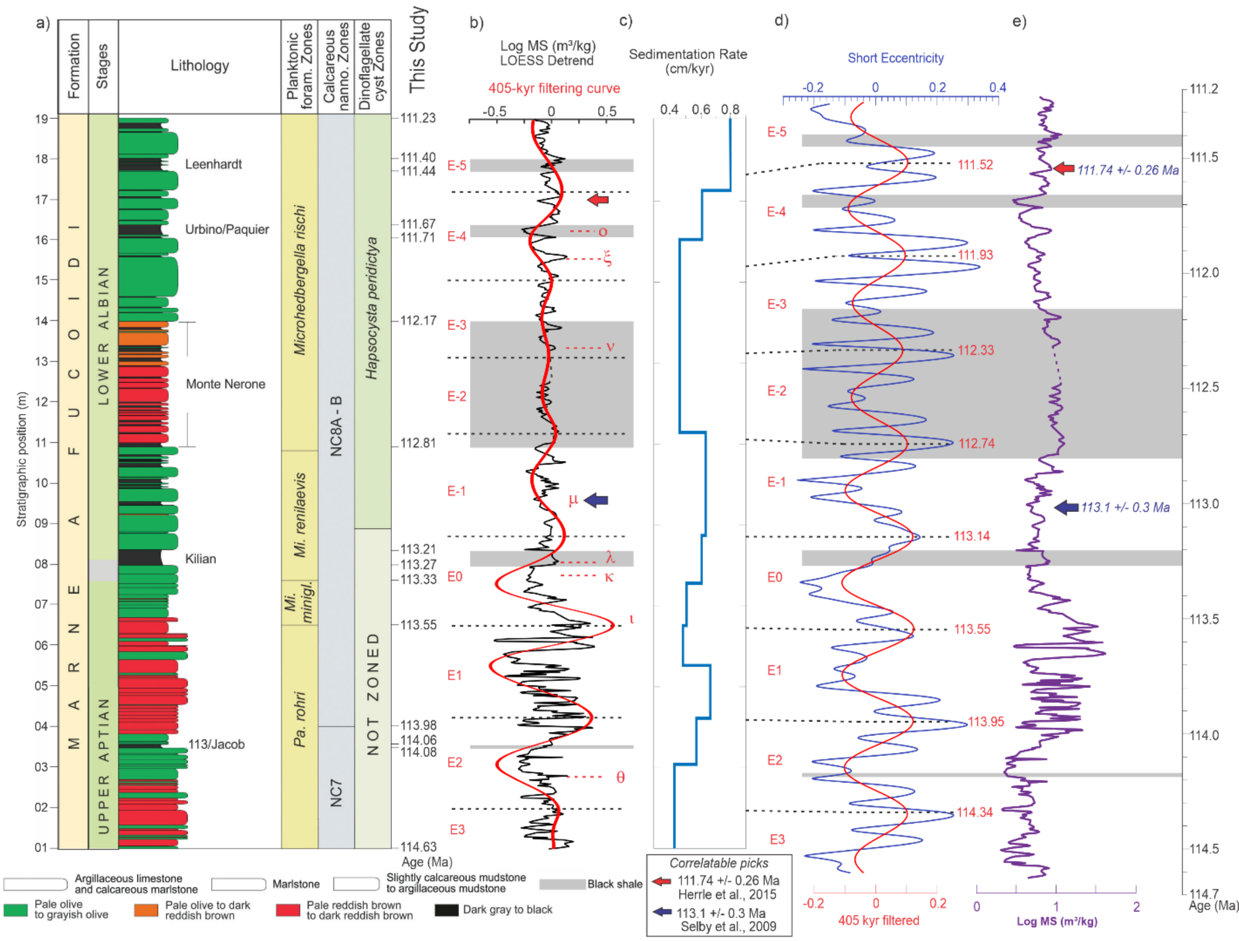



**Figure 9.** Astronomical calibration of the PLG core: a) Lithology, calcareous nannofossil and planktonic foraminiferal biostratigraphy from Coccioni et al. (2014), updated with new cyclostratigraphic ages on the right side; b) Log MS data and 405-kyr component filtered using dynamic filter, and (E) cycles denoted in red. The E-cycles and C-marks are presented in red letters and red and blue arrows represent transposed absolute ages used as tie points; c) The sediment accumulation rate (SAR) curve recovered on 405-kyr tuning (blue); d) La2004 orbital solutions (Laskar et al., 2004) for the eccentricity cycles of ~100 kyr (blue line) and ~405 kyr (red line); e) Astronomically tuned Log MS series (purple line). The major sub-events are highlighted in light grey.

## 3.8 SAR analysis

By integrating the existing biostratigraphy of the PLG section (Coccioni et al., 2014) with the transposed absolute ages (Herrle et al., 2015; Bornemann et al., 2023) and the obtained ages from our astronomical calibration, we were able to estimate a mean sedimentation rate of ~0.5 cm/kyr for the interval 1–19 m (Figure 10). This calculation was statistically tested by means of *TimeOpt* analyses (Meyers, 2015). After LOESS detrend (Figure 10a and 10b), the Log MS dataset is free from long cycles (up to 1 Myr), and values in the series become coherent with modulation and correlations parameters in TimeOpt and COCO algorithms on Acycle.

The TimeOpt analysis over all LOESS detrended series (Figure 10a, b) indicates two close possibles sedimentations rates (commonly referred to as SAR), and a $r^2$opt maximum at a SAR of 0.55 cm/kyr (Figure 10e, red). The $r^2$ envelope regression model (Figure 10f, red) suggests 0.41 cm/kyr as a SAR with maximum energy concentration, but a second large local maximum occurs between 0.5 and 0.6 cm/kyr. The $r^2$ power (Figure 10f, grey) returns *p*-values up 0.1 from 0.5-0.6 cm/kyr. The slight difference of ~0.15 cm/kyr between these SARs indicate its suitability for cyclostratigraphic analyses (Weedon, 2003). The combination of $r^2$ envelope and $r^2$ power ($r^2$ opt) estimates 0.55 cm/kyr as a best SAR (notable, an average SAR) for all intervals.

Cross-plot of the data amplitude envelope and the TimeOp*t*-reconstructed eccentricity (Figure 10g) indicate a SAR of 0.56 cm/kyr, punctuating that short-eccentricity cycles are modulated by long-eccentricity, as shown in Figure 10h-j. Similar result was found using COCO (Li et al., 2018), where correlation coefficient (Figure 10l) returns ρ-value up to 0.4 for SAR at 0.57 cm/kyr (ρ equal the Greek letter "rho"*)*. The number of contributing astronomical parameters (Figure 10m, dark blue) and the Null hypothesis (Figure 10m, red) crossing $10^{-2}$ $H_0$ significance level shows a good match at the same SAR reinforcing all previous observations. For a detailed evaluation of SAR, we applied the evolutionary versions of COCO (named eCOCO, Li et al., 2018).

eCOCO (Figure 10c) seems to better represent the SAR dependencies in tuning process (Figure 10c, blue line), with SAR's variations following the results SAR of tuning. The sedimentation rate at the base of the studied interval is 0.4 cm/kyr, which linearly increases to higher value ~0.65 cm/kyr. This pattern follows the signal present in the series of Fe and Ti data and may be associated with a change in the palaeoceanographic regime (i.e., combination of increase in run-off, input of terrigenous material and enhanced weathering) after the Cold Snap event (McAnena et al., 2013), when the warm and humid climate (typical of Cretaceous) was established. The good match between SAR, eCOCO and Ti amount (Figure 10d) strongly supports climate control, and specifically Ti amount suggests an increase in terrigenous input, which controls the deposition. The monotonous (with slight variations) interval is interrupted by a decrease of SAR (11-14m), related to the Monte Nerone mudstones and black shales. This tendency of decreasing SAR value could be observed both eCOCO and tuning's SAR data, and this regime persists upward. The Monte Nerone interval could be the result of another pulse of cold waters paced by long periods cycles, as highlighted by LOESS trend (Figure 10b, dark green line).

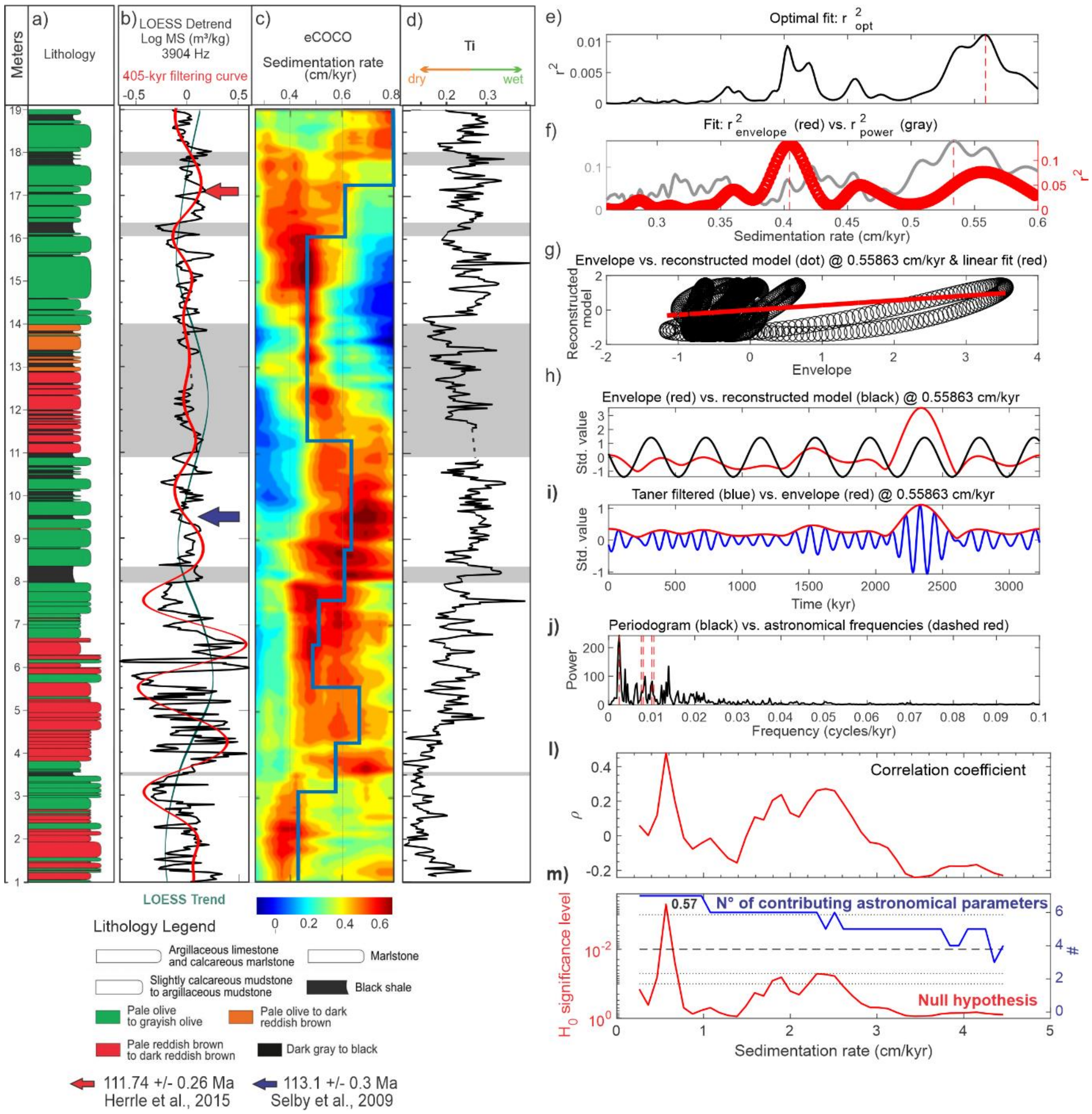



**Figure 10.** The sediment accumulation rates (SAR) analysis of the PLG core along the OAE 1b interval using TimeOpt, COCO and eCOCO methodologies: a) Lithology, described in Coccioni et al. (2014); b) LOESS trend (green line), 405 kyr signal (red line) of LOESS Log MS data (black line), presenting at least three long wavelengths cycles that were removed for the data series prior to the statistical analysis of SAR; c) eCOCO panel of LOESS detrend of Log MS data, plotted together with tuning process recovered SAR; d) Ti amount suggesting terrigenous input control of SAR; e-j) *TimeOpt* panels used for evaluating SAR in all intervals. It is notable secondary peaks due to regions within the studied interval where other rates of secondary sedimentation prevail. (l) COCO correlation coefficient with a great peak at 0.57 cm/kyr and value of ρ > 0.4. (m) The number of contributing astronomical parameters and the null hypothesis crossing $10^{-2}$ $H_0$ significance level also shows a good match with 0.57 cm/kyr SAR.

## 4 Discussion

### 4.1 Upper Aptian/lower-Albian floating astronomical timescale in the PLG core and C-isotope correlations

Our work provides a detailed upper Aptian-lower Albian time-depth framework for the PLG core. Through an astronomical calibrated age model, we are able to obtain the ages of OAE 1b sub-events and different zonal markers of calcareous nannofossils and correlated with planktonic foraminiferal zonal markers (Coccioni et al., 2012, 2014; Sabatino et al., 2015, 2018; Leandro et al., 2022). Previous studies have used a different age approach, which was based on duration of Albian Stage (Grippo et al., 2004; Huang et al., 2010). Leandro et al. (2022) used new M0r ages (Zhang et al., 2021) associated with high-precision U-Pb date of 113.1 ± 0.3 Ma (Selby et al., 2009) and provided a new age model for the Aptian with 405 kyr long-eccentricity cycle tuning based on the $g_2$-$g_5$ target curve from the La2004 solution for the Aptian–Albian.

On the other hand, using cyclostratigraphic techniques of SAR (Li et al., 2018; Meyers, 2015, 2019), we are able to estimate a sedimentation rate ranging from 0.4 to 0.6 cm/kyr for the interval 1–19 m. SAR slightly increases following the same trends of Ti and Fe contents, until the onset of the Monte Nerone black-shales cluster, where it drops below 0.5 cm/kyr and then it remains steady up to the Urbino Level. This result is consistent with the TimeOpt/COCO/eCOCO results (Figure 10).

As we used the same dataset of Leandro et al. (2022), we obtain similar SAR (mean of 0.43 cm/kyr) in the same intervals. The major difference is the tie point to anchor the 405 kyr long-eccentricity cycles, with a potential for generating a *bias* age effect. Vöhrum's tuff layer above carbon isotope negative excursion associated to the Kilian Level at Dolgen 3 core (Borneman et al., 2023) allows us to anchor the 405 kyr curve between 113.10 Ma (using the solution *La2010b* from Laskar et al., 2011b) and 113.24 Ma (using the solution *La2004*, from Laskar et al., 2004), as shown in Figure 7, providing greater precision to the tuning process since there is no longer a need to use the average value of 113.00 Ma as an anchor.

Table 2 shows estimated age for major OAE 1b sub-events. Previous studies have suggested a correlation between OAE 1a with the OJP basalt flows (Larson & Erba, 1999; Chambers et al., 2004; Tejada et al., 2009) and a rapid global warming, and elevated rates of silicate weathering both on the continents and in the oceans (Bottini et al., 2018).

However, new age constrains of the OJP show that the upper lava-flow units are much younger (i.e., 115.51–111.42 Ma) than previously suggested (Davidson et al., 2023). These numbers are consistent with our study, where the effect of enhanced weathering began near the onset of the 113/Jacob Level, marked by increasing sedimentation rate and Ti and Fe contents into the UMB. $^{187}Os/^{188}Os$ pulses related to the OAE 1b (Matsumoto et al., 2020) also support this suggestion (Figure 2). The apparent diachronism between the onset of anoxic events in different sections (e.g., Kilian at 112.9 Ma in Leandro et al., 2022 and 113.6 Ma in Fauth et al., 2022) from different global regions may be attributed to age adjustments (anchor *bias*) and $\delta^{13}C$ correlation errors, as it can be observed in Figure 8.

**Table 2:** Comparison of ages of the organic-rich levels.

Table 2 Estimated ages of the black-shale levels.

| Work | Black-shale levels (estimated age in Ma) 113/Jacob | Killian | Monte Nerone | Urbino | Leenhardt |
|---|---|---|---|---|---|
| Huang et al., 2010 | 114.2 | 112 | | | |
| Coccioni et al., 2014 | 113.2 | 111.5 | | 109.8 | >109.2 |
| Sabatino et al., 2018 | 115.0 | 112.8 | | 111.3 | >110.7 |
| Leandro et al., 2022 | 113.7 | 112.9 | | | |
| Matsumoto et al.,2020 | 114.5 | 112.8 | | 111.1 | 110.5 |
| Fauth et al., 2022 | | 113.6 | | | |
| Charbonier et al., 2023 | 114.0 | 113.2 | | | |
| This work | $114.07^{114.06}_{114.08}$ | $113.24^{113.21}_{113.27}$ | $112.49^{112.17}_{112.81}$ | $111.69^{111.67}_{111.71}$ | $111.42^{111.40}_{111.44}$ |

After comparing the ages of OAE 1b sub-events, we must double-check their stratigraphic position respect to the to our C-isotope markers (Figure 8). The 113/Jacob Level of Huang et al. (2010) occurs near the base of the *Nannoconus regularis* calcareous nannoplankton zone and within the *P. rohri* planktonic foraminiferal zone. Nonetheless, it is important to mention that these two works used different tie points: Huang et al. (2010) used the Albian-Cenomanian boundary at 99.6 Ma as a tie point for the tuning process, without using any absolute radiometric age to anchor this boundary, while Charbonier et al. (2023) employed the average age of the base of the Albian (113.2 ± 0.3 Ma by Gradstein et al., 2020, after U-Pb dating of Selby et al., 2009) in the tuning process.

The high latitude Kilian Level of Herrle et al. (2015) corresponds to the benthic *Verneuilinoides borealis* foraminiferal zone, and has a carbon isotope pattern that is quite distinct from other patterns for the Kilian Level (Huang et al., 2010; Coccioni et al., 2014;

Kennedy et al., 2014; Kennedy et al., 2017; Leandro et al., 2022; Fauth et al., 2022; Bodin et al., 2023; Charbonier et al. 2023), represented here by the **λ** marker. In general, the Kilian Level is visible in C-isotope curves as a positive excursion followed by a negative, associated with *M. renilaevis* foraminiferal zone (Kennedy et al., 2014, 2017). The Vöhrum section and the ash layer at 113.1 ± 0.3 Ma (Selby et al., 2009) do not contain planktonic foraminifera, and the correlation between the two outcrops is based on ammonite associations (top of *Hypacanthoplites jacobi* ammonite zone) and the FO of *P. columnata* (subcircular category). *H. jacobi* ammonite zone extends into the early-Albian standard zonation of Ogg et al. (2016) and could be correlated not only with the Kilian Level (Bodin et al., 2023) but also with HK 3-6 key beds (Monte Nerone, in PLG) and the Paquier Level (Herrle et al., 2010). So, the Aptian-Albian boundary in the Vöhrum section (Selby et al., 2009), does not necessarily coincide with the Kilian Level and the age of 113.1±0.3 Ma could be the age of the Ap-15, Al-1 or Al-2 carbon isotope stages (Herrle et al., 2010).

Our astronomical tuning provides an age of 112.81 Ma for the base of the Monte Nerone interval (Coccioni et al., 2014) and of 111.71 Ma for the Urbino black shale level (**o** marker), remarkably close to the U-Pb 111.74 ± 0.26 Ma of the dated and extrapolated level of Herrle et al. (2015). For the **μ** marker, the Vöhrum tuff, we estimate an age of 113.0 Ma, which corroborates the 113.1 ± 0.3 Ma of the ash layer (Selby et al., 2009; Bornemann et al., 2023). Cyclostratigraphic analysis of Nebe (1999) estimated a median age of 113.25 Ma for the Kilian Level. The present work provides an age of 113.25 Ma for the **λ** mark (extreme point of negative excursion associated to the Kilian Level, PLG core) and 113.3 Ma for the **κ** mark (extreme point of positive excursion), corroborating the 113.2 Ma age of GTS2020 (Gale et al., 2020). If we used FO of *M. renilaevis* as marker for the Aptian-Albian boundary (e.g., Gradstein et al., 2020; Kennedy et al., 2014), we extrapolated an age of 113.33 Ma. However, to facilitate global correlations (oceans and continental sections) and avoid bioevents diachronism, we suggest adopting the **κ** carbon isotope as an alternative and visual marker of the Aptian-Albian boundary.

Our FATS matches well with absolute ages (Selby et al., 2009; Herrle et al. 2015; Bornemann et al., 2023) and carbon isotope stratigraphy of the PLG core and Vocontian Basin (Coccioni et al., 2014; Herrle et al. 2004). We have been able to define a time span of 2.76 Myr for the OAE 1b event meant, from the 113/Jacob to the Leenhardt levels (Matsumoto et al., 2020). For individual sub-events, we obtain the following ages 114.07 Ma for 113/Jacob, 113.25

Ma for Kilian, 112.49 Ma for the middle part of the Monte Nerone cluster, 111.69 Ma for Urbino and 111.42 Ma for Leenhardt levels (Table 2). The estimated timespan of the 113/Jacob black-shale is quite similar to previous studies (Table 3). As this study is the first to provide a timespan of the Monte Nerone, Urbino, and Leenhardt levels in the UMB, there is no other reference to compare our estimates. These results demonstrate that our FATS reasonably matches well with the timespan of similar cyclostratigraphic studies (Leandro et al., 2022; Charbonier et al., 2023).

**Table 3:** Comparison of timespan of Upper Aptian / Lower Albian the organic-rich levels.

Table 3 Estimated timespan of Upper Aptian / Lower Albian events.

| Work | Timespan (kyr) 113/Jacob | Killian | Monte Nerone | Urbino | Leenhardt |
|---|---|---|---|---|---|
| Huang et al., 2010 | ~40 | ~120 | | | |
| Coccioni et al., 2014 | | ~200 | | | |
| Leandro et al., 2022 | ~30 | ~90 | | | |
| Fauth et al., 2022 | | ~200 | | | |
| Charbonier et al., 2023 | ~25 | ~32 | | | |
| This work | ~20 | ~60 | ~640 | ~40 | ~40 |

4.2 C-isotope stages, their markers, and sub-events levels correlations in different basins

The PLG site, where the PLG core was drilled, provides one of the most continuous, complete, and best-preserved Aptian-Albian record and is represented by calcareous pelagic rocks extending from the Albian-Cenomanian boundary down to the uppermost Barremian (Coccioni et al., 2012). Several carbon-isotope excursions are observed in the $\delta^{13}C$ record of the PLG core (Coccioni et al., 2014; Leandro et al., 2022) and have a potential for long distance correlations.

In this work, we recognize significant landmarks (notable features separating the stages or within these stages), named here as C-markers, which have been observed in other records. We reviewed eight C-isotope stages around the OAE 1b interval, based on the correlation with other sections (Figure 11). This procedure allows us to transpose the ages of significant landmarks of carbon isotope ratios, and then attribute an age to each marker and C-isotope stage.

We obtained the following ages of C-isotope stages, in stratigraphic order: **θ** = ~114.2 Ma; **ι**=~113.5 Ma; **κ**=~113.3 Ma; **λ**=~113.25 Ma; **μ**=~113.0 Ma**;** **ν**=~112.3 Ma; **ξ**=~111.8 Ma and **ο**=~111.7 Ma (Figure 11). According to these ages we suggest that the following levels can be correlated with respective counterparts in the Vocontian Basin: the Jacob/113 could be related with DC 2, the Monte Nerone Level with the HN2-HN7, and the Urbino Level with the HN13-HN15 (Figure 11). Ba/Al and Mn/Al ratios along the PLG section show two distinct peaks in the Urbino/Paquier interval (Sabatino et al., 2015). The first peak (15.6 m) represents the expression of Paquier in the PLG, while the second (16.3 m) coincides with the Urbino level, highlighting the presence of a pair of events associated with the landmark ξ.

Carbon-isotope excursions and/or organic rich-levels that define the OAE 1b have been recognized in the Tethyan and North Atlantic regions (e.g., Herrle et al., 2004, 2010, 2015; Trabucho-Alexandre et al., 2011; Kennedy et al., 2014; Coccioni et al., 2014). In the Vocontian Basin, four organic-rich levels named Jacob, Kilian, Paquier, and Leenhardt (Bréhéret, 1994) have been considered records of the OAE 1b, although some studies consider only the Jacob, Kilian, and Paquier (Trabucho-Alexandre et al., 2011) or just the Paquier (Herrle et al., 2004). The internal markers within the C-isotope stages recognized here can be used as reference to make correlations of the OAE 1b interval worldwide.

The C-isotope fluctuations could result from the balance between several processes recycling carbon on the Earth's surface, including the input of isotopically light volcanic $CO_2$, the increased recycling rates of $^{12}$C-rich intermediate water, the intensified flux of $^{12}$C-rich riverine dissolved inorganic carbon (DIC), and the thermal dissociation of methane hydrates (e.g. Menegatti et al., 1998; Weissert, 1989; Bralower et al., 1999; Matsumoto et al., 2020, 2021).

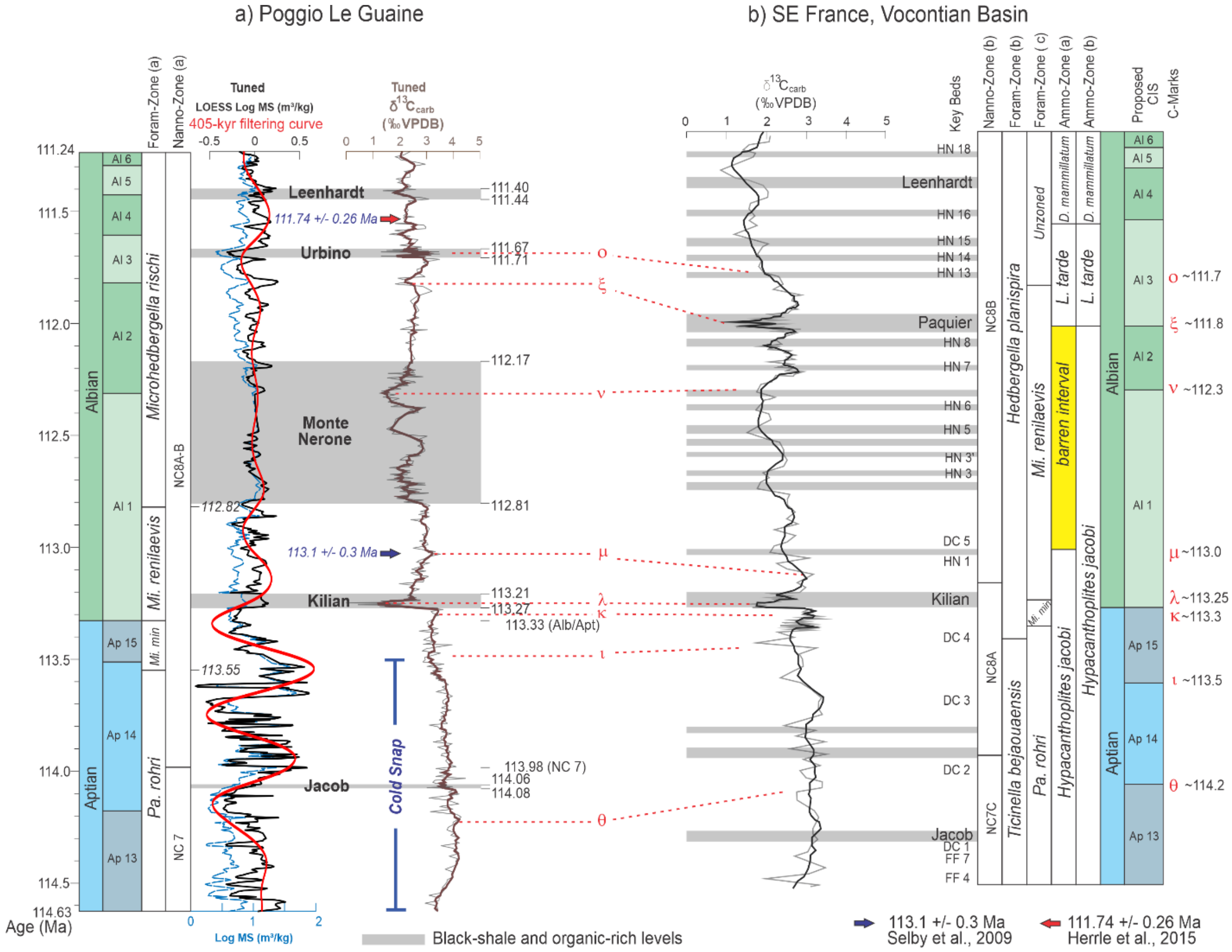



**Figure 11.** Correlation of upper Aptian-lower Albian intervals in the Umbria-Marche Basin (PLG core, on the left) with the Vocontian Basin (on the right) through $\delta^{13}C_{carb}$ records, C-isotope stages and associated markers: a) PLG foraminiferal and nannofossil zones from Coccioni et al. (2014); b) Foraminiferal and nannofossil zones from Herrle et al. (2004); b-c) Foraminiferal zone and ammonite zone from Charbonier et al. (2023) and a) Ammonite zone from Bodin et al. (2023).

The combined isotope stratigraphy of Poggio le Guaine, Vocontian Basin, DSDP Site 545, and ODP Hole 1049C records (Coccioni et al., 2014) allows us to characterize the studied interval on global scale. The new C-isotope correlation allows us to precisely calibrate the absolute age (111.74 ± 0.26 Ma for **o** marker) to be transposed into the PLG record and used as a tie-point for a new cyclostratigraphic tuning of entire studied interval. Previous studies used $^{206}Pb/^{238}U$ age of 113.1 ± 0.3 Ma determined for chemically abraded zircon from a tuff horizon 65 cm above the Aptian/Albian boundary (Selby et al., 2009) as a tie-point for the 405 kyr cycles tuning, but the tuff horizon near top *H. jacobi* ammonite zone in the Schwicheldt Ton Member, Gault Formation (Vöhrum, Germany) was ~1000 km distant from the PLG site. Furthermore, the very top of this ammonite zone has been reported in different positions (Herrle et al., 2010; Charbonier et al., 2023; Bodin et al., 2023) and could not be correlated with a specific C-isotope stage. The top of the *H. jacobi* zone is not the best anchoring point for cyclostratigraphic studies, as it has an unconstrained age and thus cannot be correlated with the Kilian Level (Bodin et al., 2023); the Paquier level (Herrle et al., 2010) and the Leenhardt level (Charbonier et al., 2023), Figure 11b.

Bornemann et al. (2023) presented the first high-resolution CIS for the Berriasian to Coniacian interval from NW Germany that stratigraphically locates the position of the Vöhrum boundary tuff (**μ** marker) in a carbon isotope curve and proposed a slightly older age for the Aptian–Albian boundary of ca. 113.65 Ma. This estimate of the Kilian age (**λ** marker) was anchored on the cyclostratigraphic study of Nebe (1999), which provided a sedimentation rate of 3.6 cm/kyr and extended upwards 20 m of section (interval between tuff and Kilian) to conclude that the Kilian event is 555 ± 13 kyr older than the tuff. As the tuff horizon was dated at 113.1 ± 0.3 Ma (Selby et al., 2009), then the Kilian must have an age of 113.66 ± 0.3 Ma.

We conclude that transposing the **o** marker to the 111.74 ± 0.26 Ma age and test the range of possible ages of the **μ** marker is more realistic and reliable than transposing the top of the *H. jacobi* zone found in Vöhrum as marker of the Aptian-Albian boundary (Gale et al., 2020).

Even at a great distance and with the absence of bioevents common to both basins, the CIS provides: 1. the association of 111.74 ± 0.26 Ma age (**o** marker) obtained in Axel Heiberg (Herrle et al., 2015) to the OAE 1b event described on Gradstein et al. (2012), understood here as a correlation to the Urbino/Paquier at the UMB (Coccioni et al., 2012, 2014; Sabatino et al., 2015, 2018), 2, the association of tuff horizon position (**μ** marker) at the end of the **λ** excursion as 113.1 ± 0.3 Ma (Selby et al., 2009) and 3. the association of 113.66 ± 0.3 Ma for the Kilian (***k*** marker).

### 4.3 Paleoclimate during OAE 1b event

Paleoceanographic changes during the OAE 1b show that each level enriched in organic matter has its own characteristics, with distinct detrital input values, different types of organic matter, and varying degrees of anoxia and productivity (Erbacher et al., 1999; Sabatino et al., 2015, 2018; Heimhofer et al., 2006; Matsumoto et al., 2022; Bodin et al., 2023). Likely, different geological processes controlled the depositions of the black shales, resulting in a wide range of variables and forcing possibilities (Table 4). However, the long lasting interval encompassing this highly variable period, sometimes simplified by the concatenation and naming of various distinct events by the acronym OAE 1b, leads us to attribute a volcanic origin background of Kerguelen Plateau, Broken Ridge and/or OJP (Frey et al., 2000; Whitechurch et al., 1992: Sabatino et al., 2015; Davidson et al., 2023) or a long-term orbital cycle (longer than 2 Myr) or even the effect of orbital chaotic resonance (Ma et al., 2017).

Sabatino et al., (2015) concluded that the enhanced burial of barium in the latest Aptian–early Albian could reflect higher marine primary productivity, which is presumably driven by higher atmospheric $pCO_2$, enhanced terrestrial weathering and additional nutrient delivery to the ocean and, suggested that the negative excursions in the $\delta^{13}C_{carb}$ in the Kilian and Urbino/Paquier levels could be related to a major contribution of isotopically light terrestrial carbonate ions by an enhanced continental runoff during more humid conditions, as clearly testified by the detrital proxies (Sabatino et al., 2015).

The PLG Aptian-Albian sediments were deposited during an exceptionally warm climate (Sabatino et al., 2015), with short term cold episodes (McAnena et al., 2013; Bottini et al., 2015; Bodin et al., 2023; Herrle et al., 2015). Some pieces of evidence support the relative short-term glacial intervals such as glendonites and deposits with affinities to glacial tillites and dropstones (Price, 1999). Our correlation based on C-isotope positions *Glendonites beds* of Axel Heilberg Island (Herrle et al., 2015) and the concurrent Cold Snap event (McAnena et al, 2013) at the PLG support the existence of cool shelf waters during late Aptian age. The basal interval of studied section of the PLG, described as Cold Snap (McAnena et al, 2013; Bottini et al., 2015; Leandro et al., 2022), is dominated by lowest levels of titanium until the planktonic foraminiferal turnover.

It is noteworthy that there is a mismatch between the peaks of Hg/TOC and levels enriched in organic matter (Sabatino et al., 2018). Also, the peaks of volcanism associated with the OAE 1b event occur only in the initial portion of the event, with a non-volcanic character being attributed to the majority of OEA 1b (Matsumoto et al., 2022), suggesting that volcanism (and the extreme climatic conditions associated with these events) are not the cause of the deposition of these levels, but rather an amplifying component of the orbital forcing that conditioned the generation of intense monsoon events and high weathering, as supported by the relationship between some enriched levels and weathering proxies. These arguments lead us to agree with the *multiple drives* mechanism proposed by Wang et al. (2022) for atmospheric-circulation reorganization.

In the PLG core series, the $CaCO_3$ curve follows a long cycle with an inverse trend respect to MS. Except from the Urbino/Paquier interval, all black shales are depleted in $CaCO_3$ reflecting fluctuations in carbonate productivity and terrigenous sediment supply. Between the Jacob Level and the planktonic foraminiferal turnover, there is an interval with high values of $CaCO_3$ and MS that could be ascribed to a deposition in a different environmental context (higher level of MS associated with high $CaCO_3$ content, a feature opposite to the entire rest of the studied interval), relative to the climax of the *Cold Snap* event (e.g., McAnena et al., 2013; Bottini et al., 2015; Leandro et al., 2022) and abnormally enriched with Mn/Al (Sabatino et al., 2015). This oscillation of ~0.5 Myr in the $CaCO_3$ data is related to an increase of MS and indicates a paleoclimatic control that changes the total amount of magnetic particles or the magnetic carrier. It is notable the presence of high orders cycles in the $CaCO_3$ data, likely associated with episodes of enhanced carbonate dissolution (Broecker and Clark, 1999).

The Ti and Fe contents are inferred here as proxies for arid and humid phases. The relationship between the phases of the signals of MS, Fe, Ti, and $CaCO_3$ suggests a common paleoclimatic control, where the orbital forcing is amplified by stochastic occurrences, corresponding to volcanic episodes and rapid atmospheric $CO_2$ input (Sabatino et al., 2015; Matsumoto et al., 2020, 2022). Heimhofer et al. (2006), on the basis of a strong increase in terrestrial palynomorphs, interpreted that the beginning of OAE 1b event in the Vocontian Basin as being primarily formed by detrital inputs from the land detrital components. Arid conditions during the late Aptian–early Albian interval with more humid condition in the uppermost Aptian

Kilian and early Albian Urbino/Paquier levels (Sabatino et al., 2015) could be a key to understand the cause (s) for organic-rich levels deposition.

Wavelengths analysis (Figures 4 and 5) suggest three different cycles, with different periods, forcing the paleoclimate: the first one, a long-period wavelength (combination of Myr cycles with 1600, 1000 and 700 kyr) with minimal values associated with Cold Snap and Monte Nerone intervals; the second wavelength that provides the alternation of carbonate bundles with black shales could be also observed in the upper section; and a third one with higher frequency, with time durations similar to those observed in the deposition of black shales. The Kilian and Leenhardt levels are positively correlated with short-term oscillations in both XRF proxies, highlighting that the increased continental sediment input, contributed to the deposition of these lithofacies. On the other hand, no relationship between increased continental input and the 113/Jacob and Urbino/Paquier levels was found. The long-term variations in Hg/TOC values associated with peaks could document that the effects of significant Hg emissions are related to the multi-phase emplacement of volcanism during the Aptian-early Albian (Sabatino et al., 2018), is probably the responsible for the termination of the arid and relatively cool conditions of the Cold Snap (McAnena et al, 2013; Wang et al., 2022).

A synthesis of studies related to the organic-enriched levels that are part of OAE 1b highlights the various mechanisms and forcings responsible for the deposition of these levels (Table 4). The variables indicate that the Jacob/113 subevent is clearly a 'volcanic' event that resulted in high productivity, as shown by volcanic indicators and the absence of weathering indicators. Pyrolysis analyses reveal that the Jacob Level is composed of continental-origin organic matter in the Vocontian Basin (Bodin et al., 2023). However, in the PLG, a significant marine contribution is present (Sabatino et al., 2015), highlighting paleogeographic control.

The Kilian subevent presents a mixed character (volcanic + monsoonal), as both the presence of continental organic matter and precursor eruptions, along with the ages of preferential plagioclases, suggest that its deposition must have been conditioned by both the induced effect of volcanic activity and the result of changes in Hadley circulation dynamics. This forced large-scale precipitation and stratification of the water column, marking the end of the Cold Snap period. In contrast to the Jacob subevent, the organic matter present in the Kilian Level is of continental origin in the PLG. However, in the Vocontian Basin (Briers section), it exhibits a substantial marine content with increased primary productivity (Bodin et al., 2023).

The cluster related to the Monte Nerone interval is very enigmatic and seems to have a mixed character. The sediments become more reddish and argillaceous, giving this interval a CORB-like characteristic (Wang et al., 2009; Coccioni et al., 2014). The high frequency of lithological intercalation, associated with sporadic inputs of terrestrial material, suggests a monsoonal character. However, the lack of correlation between volcanic indicators does not allow for a perfect characterization of this interval as volcanic.

**Table 4:** Synthesis of organic matter-rich levels paleoceanographic proxies' indicators.

| | Detrital input proxies | | Volcanism indicators | | | Productivity | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Organic Matter-Type (b.) | Fe, Ti (a.) | $^{187}Os/^{188}Os$ (c.) | Hg/TOC (d.) | Plag. Ages(f.) | HI values (b.) | Aeolian input(b.) | M. palnk. archaeal (b, e.) | Ba content (a.) |
| *onset* | | | Yes? | Yes | Yes | | | | Median |
| *Jacob Level* | II (Marine contrib.) and III | Low | Yes | No | Yes | High | Yes | | Median |
| | | | | | | | | | |
| *onset* | | | Yes | Yes | Yes | | | | High |
| Kilian | III and IV (Terrestrial) | High | No | No | Yes | Low | Yes (top) | Yes | Low |
| | | | | | | | | | |
| *onset* | | | No | Yes | No | | | | High |
| M. Nerone | III and IV (Terrestrial) | es (sporadi | No | Yes (sporadic) | Yes | Low | | | Median |
| | | | | | | | | | |
| *onset* | | | No | No | Yes | | | | High |
| Urbino/Paquier | II (Marine contrib.) | No | No | No | Yes | High | | yes | High |
| | | | | | | | | | |
| *onset* | | | No | Yes | Yes | | | | Median |
| Leenhardt | III and IV (Terrestrial) | High | No | No | No | Low | | | Low |

a = This study; b = Sabatino et al., 2015; c= Matsumoto et al., 2022; d = Sabatino et al., 2018; e = Kuypers et al., 2002; f = Davidson et al., 2023

Despite the suggestion of disconnection between the Urbino and Paquier levels, at this point, given the level of detail in the studies conducted so far, we will treat them as similar intervals, as even the Paquier Level could be subdivided into two events (Erbacher et al., 1999; Kuypers et al., 2002). The clear marine contribution, evidenced by the presence of marine planktonic archaea, high productivity, extreme redox conditions (presence of redox-sensitive elements), very high thallium isotope values (Wang et al., 2022), and the absence of volcanic indicators would result in a characterization of this level as an example of a monsoonal global anoxic event. However, the lack of detrital input indicators suggests that the Paquier Level is likely associated with a major transgressive event, unlike the Leenhardt Level, which is characterized as a clearly monsoonal event (terrestrial organic matter and high values of proxies related to weathering and humidity), combined with a volcanic event, as shown by volcanic indicators, as in Table 4.

We conclude that the Cold Snap period, characterized by milder temperatures compared to the average of the Cretaceous period, comes to an end due to the input of volcanic $CO_2$ resulting from the implementation of Large Igneous Provinces (LIPs), initiating a period of hyperthermia, heavy precipitation, intense weathering and marine primary productivity. The significant input of continental material resulting from weathering conditioned the deposition of organic-rich levels during the OAE 1b event. In chaos theory, the effect where a small change in one variable can cause significant and amplified changes in other variables is known as the "butterfly effect." Large volcanic eruptions likely played this role in paleoclimate during OAE 1b, acting as "stochastic noise" in the nonlinear paleoclimatic dynamic system. Rapid marine transgressions and atmospheric disturbances related to these peaks of volcanism served as amplifiers of orbital forcings, resulting in deoxygenation and carbon burial events deposited during OAE 1b.

## Conclusions

A cyclostratigraphic analysis was performed on the MS, Ti and Fe series of the upper Aptian-lower Albian interval from the PLG core, encompassing the pelagic Marne a Fucoidi succession of the Umbria-Marche Basin (Central Italy), which is one of the most detailed sedimentary record of this period. The new temporal calibration through the metric imposed by orbital cycles allows us to better correlate the paleoceanographic fluctuations within the OAE 1b interval with their respective forcings. On the basis of these, we provide evidence of:

1. MS, Ti and Fe data-set display a 405-kyr cycles a strong and statistically significative (> 95% CL) signal that correlates with the long-eccentricity Milankovitch cycle. Our interpretation is supported by SAR statistical tests (TimeOpt and COCO/eCOCO methodologies) resulting in an average rate of 0.5 cm/kyr. There is an evident control of SAR by weathering and terrigenous input as revealed by Ti profile.
2. By combining new biostratigraphic and high-resolution isotopic data, a 405-kyr calibrated floating astronomical timescale was constructed for the PLG core, and we can infer an age of ~113.55 for the FO of *M. miniglobularis* (6.5 m), ~113.33 Ma for the FO of *M. renilaevis* (7.7 m) and ~112.82 Ma for the FO of *M. rischi* (10.8 m).
3. Our astronomical calibration shows ~7 cycles of 405 kyr in the interval between 3.5-18 m (OAE 1b interval), which covers a timespan of ~2.68 Myr. The chronostratigraphic study also provides an age of 114.07 Ma for 113/Jacob 113.25 Ma for Kilian, 112.49 Ma as a central age of the Monte Nerone cluster, 111.69 Ma for Urbino and 111.42 Ma for

Leenhardt sub-events, and a timespan of ~20 kyr for 113/Jacob, 60 kyr for Kilian, 640 kyr for Monte Nerone cluster, 40 kyr for Urbino and 40 kyr for Leenhardt levels.

4. C-isotope stratigraphy shows an immense potential for be used as tie point for cyclostratigraphic studies and becomes a valuable way to evaluate diachronism of bioevents, allowing correlation between different basins through c-marks, with ages estimated using PLG core tuning as: $\boldsymbol{\theta}$ = ~114.2 Ma; $\boldsymbol{\iota}$=~113.5 Ma; $\boldsymbol{\kappa}$=~113.3 Ma; $\boldsymbol{\lambda}$=~113.25 Ma; $\boldsymbol{\mu}$=~113.0 Ma**;** $\boldsymbol{\nu}$=~112.3 Ma; $\xi$=~111.8 Ma and **ο**=~111.7 Ma, suggesting that: Jacob/113 PLG level could be related with DC 2 of Vocontian Basin; Monte Nerone PLG level with HN2-HN7 Vocontian Basin levels and; Urbino PLG level with HN14-HN15 Vocontian Basin levels.
5. Each strata within the OAE 1b event exhibits distinct characteristics arising from the interplay of a warm climate induced by volcanic CO2 input (which acts as an amplifier of orbital forcings, driving paleoclimate changes) and oceanic-atmospheric disturbances such as heavy precipitation and intense weathering. These factors contribute to deoxygenation and carbon burial during the OAE 1b period.

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## Open Research

MS, Ti and Fe data archiving process is already underway in the ZENODO repository (DOI 10.5281/zenodo.10557295.), where the temporary upload of a copy of your data is being carried out for review purposes.

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