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ASTRONOMICAL CONSTRAINTS ON THE DURATION OF THE EARLY JURASSIC PLIENSBACHIAN STAGE AND GLOBAL CLIMATIC FLUCTUATIONS

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ABSTRACT

The Early Jurassic was marked by multiple periods of major global climatic and palaeoceanographic change, biotic turnover and perturbed global geochemical cycles, commonly linked to large igneous province volcanism. This epoch was also characterized by the initial break-up of the super-continent Pangaea and the opening and formation of shallow-marine basins and ocean gateways, the timing of which are poorly constrained. Here, we show that the Pliensbachian Stage and the Sinemurian–Pliensbachian global carbon-cycle perturbation (marked by a negative shift in δ^{13}C of 2–4‰), have respective durations of ~8.7 and ~2 Myr. We astronomically tune the floating Pliensbachian time scale to the 405 Kyr eccentricity solution (La2010d), and propose a revised Early Jurassic time scale with a significantly shortened Sinemurian Stage duration of 6.9 ± 0.4 Myr. When calibrated against the new time scale, the existing Pliensbachian seawater ^{87}Sr/^{86}Sr record shows relatively stable values during the first ~2 Myr of the Pliensbachian, superimposed on the long-term Early Jurassic decline in ^{87}Sr/^{86}Sr. This plateau in ^{87}Sr/^{86}Sr values coincides with the Sinemurian–Pliensbachian boundary carbon-cycle perturbation. It is possibly linked to a late phase of Central Atlantic Magmatic Province (CAMP) volcanism that induced enhanced global weathering of continental crustal materials, leading to an elevated radiogenic strontium flux to the global ocean.

[1] INTRODUCTION

The Early Jurassic (201.4–174.1 Ma) is distinguished by the end-Triassic mass extinction and global warming event, climatic cooling in the Late Pliensbachian and subsequent greenhouse warming in the Early Toarcian (McElwain et al., 1999; Hesselbo et al., 2002; Ruhl et al., 2011; Gradstein et al., 2012; Wotzlaw et al., 2014; Gomez et al., 2015; Korte et al., 2015). Continental rifting and the break-up of Pangaea in the Early Jurassic led to the formation of continental and marine rift basins, which acted as major sites of organic carbon burial and led to the generation of hydrocarbon source rocks (Fleet et al., 1987; Olsen, 1997). The equatorial Tethys Ocean was connected in the Early Jurassic (Sinemurian) to Eastern Panthalassa via the Hispanic Corridor and to the high-latitude Boreal realm via the Viking Corridor, likely initiating changes in (global) ocean currents and planetary heat distribution (Figure 1; Porter et al., 2013; Korte et al., 2015).

The Early Toarcian in particular was set apart by the global Toarcian Oceanic Anoxic Event (T-OAE), with possibly the largest exogenic carbon-cycle perturbation in the Mesozoic, and associated perturbations in other global geochemical cycles, palaeoclimate and the palaeoenvironment, linked to emplacement of a large igneous province (LIP) in the Karoo-Ferrar region (Jenkyns, 2010; Burgess et al., 2015; Percival et al., 2015). The Early Jurassic was also marked by multiple somewhat smaller scale fluctuations in the global exogenic carbon cycle (Riding et al., 2013; Jenkyns and Weedon, 2013), shifts between climatic warming and cooling on regional and global scales (Korte et al., 2009; Korte and Hesselbo, 2011; Korte et al., 2015), marine and continental extinction and origination events (Close et al., 2015), and fluctuations in regional and global sea-level (Hallam, 1997; Hesselbo et al., 2004, 2008). The age, rate of change, and duration of these events are, however, poorly constrained and their inter-relationships only crudely appreciated.

Here, we determine the age and duration of the Early Jurassic Pliensbachian Stage and ammonite zones and subzones in the hemipelagic marine sedimentary record of the Mochras Farm (Llanbedr) Borehole from west Wales (Cardigan Bay Basin). The Mochras Borehole represents ~1300 m of possibly the most continuously deposited and stratigraphically expanded Lower Jurassic sedimentary archive known (Figure 2; Hesselbo et al., 2013). High-resolution (sub-precession scale) element concentration data from this cored material are used to construct a floating astronomical time scale for the Early Jurassic Pliensbachian Stage. Combined with published astrochronological and radiometric constraints on the age of the Rhaetian–Hettangian (Triassic–Jurassic) and Pliensbachian–Toarcian Stage boundaries, and astrochronological constraints on the duration of the Hettangian and Toarcian Stages, we calculate the duration and age of the Pliensbachian Stage and its constituent zones. With these data, we then assess the duration and rate of change of the Sinemurian–Pliensbachian climatic and global carbon-cycle perturbations and the Late Pliensbachian climatic cooling cycles, and assess the rate of change of Pliensbachian seawater $^{87}Sr/^{86}Sr$.

[2] THE MOCHRAS FARM (LLANBEDR) BOREHOLE

The Mochras Farm (Llanbedr) Borehole, hereafter referred to as Mochras, was drilled in 1968–1970 on the west coast of Wales (52°48’32” N, 4°08’44” W; Figure 1; Woodland, 1971; Dobson and Whittington, 1987; Hesselbo et al., 2013; Copestake and Johnson, 2014). The borehole yielded, unexpectedly, a ~1.3 km-thick (601.83–1906.78 m below surface), biostratigraphically complete succession of calcareous mudstone and clay-rich limestone, representing almost the complete Early Jurassic, an interval representing some 27 Myr of geological time.

The Early Jurassic age sedimentary record in the Mochras core is more than twice as thick as any other UK core or coastal outcrop, and it is over four times more expanded than the well-studied Sancerre–Couy core from the Paris Basin, France (Figure 2; Tappin et al., 1994; Hesselbo et al., 2013; Boulila et al., 2014). The Hettangian and Sinemurian part of the Mochras core was largely broken up for ammonite biostratigraphy; hence only limited continuous core is preserved for these stages. Continuous core slabs are, however, preserved for the Pliensbachian and Toarcian parts of Mochras (Hesselbo et al., 2013).

[3] BIO- AND CHEMOSTRATIGRAPHY

Biostratigraphical zones, combined with high-resolution geochemical proxy records, provide the primary means for global correlation of Lower Jurassic marine and terrestrial sedimentary archives. The Pliensbachian Stage in northwest Europe is subdivided into five ammonite zones (and 15 ammonite subzones), which are all present and recognized in the Mochras core (Ivimey-Cook, 1971; Page, 2003; Copestake and Johnson 2014). In this paper, these are referred to as zones and subzones, and are named by the index species name (e.g. *margaritatus* zone). Foraminifers provide further biostratigraphical constraints, and allow detailed correlation to records elsewhere (Copestake and Johnson, 2014).

The Pliensbachian is further marked by perturbations of global geochemical cycles and climate. A 2–4‰ negative shift in the carbon-isotope composition ($\delta^{13}C$) of skeletal (belemnite) calcite, bulk shallow-water carbonate, and organic matter is recognized at the Sinemurian–Pliensbachian boundary at Robin Hood's Bay (Yorkshire, UK), the Central Apennines and Trento Platform (Italy), in Portugal and Germany, and in the Mochras core (Jenkyns et al., 2002; Morettini et al., 2002; van de Schootbrugge et al., 2005; Woodfine et al., 2008; Korte and Hesselbo, 2011; Franceschi et al., 2014). This negative carbon-isotope excursion (CIE) likely represents a global carbon-cycle perturbation and associated climatic change, and allows detailed stratigraphical correlation, potentially at a resolution equivalent to, or even significantly higher than, ammonite zones. The Late Pliensbachian was marked by a major positive shift, of up to 5‰, in the $\delta^{13}C$ of wood ($\delta^{13}C_{WOOD}$), and up to 3‰ in the $\delta^{13}C$ of organic matter ($\delta^{13}C_{TOC}$; TOC: Total Organic Carbon) (Figure 7; Suan et al., 2010; Korte & Hesselbo, 2011; Silva et al., 2011), reflecting enrichment of ^{13}C in the coupled ocean-atmosphere carbon pool, and thus a perturbation of the global carbon cycle. This carbon-cycle perturbation determined from the upper *margaritatus* zone, correlates with regionally identified sea-level fluctuations and associated changes in shallow-marine $\delta^{18}O_{CALCITE}$, possibly reflecting climatic cooling cycles under conditions of massive carbon burial, with an enhanced flux of organic matter from the ocean-atmosphere system to the sedimentary carbon pool (Korte and Hesselbo, 2011). Alternatively, regional cooling may have resulted from an early phase of obstruction of the Viking Corridor, leading to decreased seawater temperatures across northwest Europe (Korte et al., 2015). The observed Pliensbachian perturbations in global geochemical cycles allow for detailed high-resolution stratigraphical correlation between geographically separated sedimentary archives from both the marine and terrestrial realms.

[4] ANALYTICAL METHODS

High-resolution (10–15 cm) elemental concentrations (e.g. Ca, Fe, Ti) were obtained by hand-held X-ray fluorescence (XRF) analyses on the slabbed archive half of the Mochras core, from the Upper Sinemurian *raricostatum* zone to the Lower Toarcian *tenuicostatum* zone (1284.08–861.32 m). Rock-Eval analysis, providing Total Organic Carbon (TOC) content, Hydrogen Index (HI) values and % Mineral Carbon, was performed on ~50 mg of homogenized sample, with the Rock-Eval VI unit from Vinci Technologies, at the department of Earth Sciences, University of Oxford. Analysis of $\delta^{13}C_{TOC}$ was performed on decarbonated and homogenized Late Pliensbachian age outcrop samples from Staithes (Yorkshire, UK), utilising ammonite biostratigraphy for correlation to the Mochras core (Figure 7). Detailed methodology and data quality control are described in the Supplementary Online Materials.

[5] RESULTS AND DISCUSSION

[5.1] SEDIMENTARY RHYTHMS IN THE PLIENSBACHIAN OF MOCHRAS

The Pliensbachian in the Mochras core shows metre-scale lithological couplets of pale grey limestone and dark brown to grey, locally faintly laminated, mudstone, with individual couplets commonly showing gradual transitions between these end-members (Figure 3). The lithological expression of these couplets does, however, vary, in some cases being represented by calcareous mudstone (commonly also more silty) alternating with locally darker, shaly mudstone. These primary lithological cycles occur throughout the Pliensbachian in the Mochras core and vary in thickness between ~30 cm (e.g. latest Pliensbachian) and ~90 cm (e.g. Early Pliensbachian), with individual carbonate beds measuring 20–40 cm (reduced to 5–20 cm in the Late Pliensbachian) (Figures 3, 4). The lithological couplets are especially pronounced at the Sinemurian–Pliensbachian transition (base *jamesoni* zone) and the top *ibex* to base *margaritatus* zones where they comprise carbonate-poor mudstone with moderate organic-matter content (TOC: ~0.9–2.1%) and carbonate-rich mudstone or limestone ($CaCO_3$: ~10–65%) with reduced organic-matter content (Figures 3, 4; Supplementary Figure 2).

Individual lithological couplets are generally symmetrical in nature, with little indication of depositional hiatus or scouring (Figure 3). The more organic-rich lithology is commonly dark grey and faintly laminated on a millimetre scale, particularly in the lowermost Pliensbachian part of the core, whereas the more carbonate-rich lithology is commonly thoroughly bioturbated (Figure 3). Thin-section analysis shows evidence for early diagenetic processes, such as calcite replacement and cementation (Supplementary Figure 3), possibly resulting from the degradation of organic matter and the associated reduction of sulfate, as evidenced by the occurrence of pyrite framboids. However, we exclude the possibility that the lithological couplets are solely related to diagenesis, and interpret them as depositional in origin, as supported by the burrow mottling, with dark-pale and pale-dark mixing of primary sediments (cf. Hallam, 1986). Furthermore, fluctuations in HI values of the bulk sedimentary organic matter closely match the observed variations in $CaCO_3$, suggesting a climatic control on periodic fluctuations in the supply of organic and inorganic matter to the seabed (Supplementary Figure 2), similar to that observed for the Upper Jurassic Kimmeridge Clay Formation at Kimmeridge Bay (UK) and the Lower Jurassic Blue Lias Formation in southern England (Weedon, 1985; Waterhouse, 1999; Weedon et al., 1999; Clemence et al., 2010; Ruhl et al., 2010). Alternatively, observed drops in HI values may have resulted from the oxidative removal of marine algal organic matter in better-oxygenated conditions in the water column and/or sedimentary pore space.

Lithological couplets of similar character have also been observed for coeval Pliensbachian successions in other marine basins across the UK (e.g. Sellwood, 1970, 1972; van Buchem and McCave, 1989; van Buchem et al., 1992, 1994; Hesselbo and Jenkyns 1995; Weedon and Jenkyns, 1999). For example, lithological changes in the Mochras core closely resemble the time-equivalent Belemnite Marl Member (Charmouth Mudstone Formation) in outcrops on the Dorset coast, southern England, where individual beds and distinct calcareous mudstone-shale couplets are laterally continuous for over 2 km (Hesselbo and Jenkyns, 1995; Weedon & Jenkyns, 1999), suggesting chronostratigraphical significance and a stable allogenic forcing mechanism, likely to be high-frequency climate change. The latest Sinemurian and Pliensbachian sedimentary sequence in the Mochras core also shows similar periodic alternations in lithology relative to the coeval shallow-marine Redcar Mudstone Formation at Robin Hood's Bay, although these latter sediments are characterized by silty to very fine sandy mudstone beds alternating with silty mudstone and shale, with common levels of concretionary siderite, and which were interpreted to originate from changes in storm frequency (van Buchem & McCave, 1989; van Buchem et al., 1992, 1994; Hesselbo and Jenkyns 1995; van Buchem and Knox, 1998).

[5.2] MILANKOVITCH-CONTROLLED SEDIMENTARY PERIODICITIES IN THE PLIENSBACHIAN OF THE MOCHRAS CORE

The observed decimetre- to metre-scale amplitudinal change in calcium concentration determined by XRF directly reflects the observed lithological couplets (in $CaCO_3$) and is especially prominent around the Sinemurian–Pliensbachian boundary (*raricostatum* and *jamesoni* zones) and in the late Pliensbachian *margaritatus* zone (Figures 3, 4), illustrating a strong modulation by long-term periodicities. Iron (Fe) and titanium (Ti) concentrations in the Mochras core also fluctuate strongly and both are largely negatively correlated with the calcium concentration (Figure 3), suggesting simple sedimentary carbonate dilution. However, different climatic controls on detrital element supply or diagenetic element enrichment may also have affected the carbonate-silicate balance. It is reasonable to conclude that diagenesis exerted some control on the distribution of carbonate, likely enhancing the primary lithological cyclicity inferred from sedimentary structures, trace fossils, and other palaeontological characteristics outlined above. The observed fluctuations in calcium concentrations therefore partly reflect relative changes in the particulate carbonate flux, together with diagenetic effects that also have their origins in a primary palaeoenvironmental cyclicity that may have occurred over Milankovitch time scales.

The XRF-based Ca-concentration data series, combined with the stacked core-photographs allow for the initial visual identification of calcareous beds and associated lithological couplets. These lithological couplets are not evenly spaced, but occur in bundles (E^1) of 4–5 sedimentary rhythms. Within a bundle the more calcareous beds generally thicken up-section and become more pronounced, forming a weakly asymmetric cycle (Figures 3, 4). Generally, four of these smaller bundles (E^1), each consisting of 4–5 lithological couplets, occur in one super-bundle (E^2). The observed couplets, bundles (E^1) and super-bundles (E^2) can generally be recognized throughout the core, but vary in thickness, probably due to minor changes in sedimentation rate (Figure 4). The ratio between the thickness of the couplets, the bundles and the super-bundles is, however, constant, consistent with a stable forcing mechanism, which we interpret as a climatic control operating on Milankovitch frequencies.

The lithological couplets in the coeval Belemnite Marl Member in Dorset are suggested to represent ~21 Kyr precession cyclicity (Weedon & Jenkyns, 1999). Following this interpretation, we assign ~100 and ~405 Kyr eccentricity periodicities to the visually defined bundles (E^1) and super-bundles (E^2) (Figures 3, 4). This procedure allows for independent comparison to Milankovitch periodicities assigned from subsequent spectral and multi-taper analyses. Some of the E^1-bundles are, however, marked by only two lithological couplets that are generally thicker and more carbonate-rich, and which consistently occur only during the minimum between two E^2-bundles (Figure 4). Following the above, they may reflect a change from dominant eccentricity-modulated precessional forcing to obliquity forcing.

[5.3] SPECTRAL & MULTI-TAPER ANALYSES

The XRF elemental data obtained from the Pliensbachian of the Mochras core were manipulated to uniform sample spacing using linear interpolation. For spectral analyses, the series were analyzed with the 3π multi-taper method (MTM) using the Astrochron toolkit (Meyers, 2014; R Package for astrochronology, version 0.3.1), with robust red noise models (Mann and Lees, 1996), and with AnalySeries 2.0.8 (Paillard et al., 1996). Initial spectral analysis was performed with AnalySeries on a detrended data series (with low band-pass filtering to remove periodicities >150 m). Dominant spectral components (Supplementary Figure 4) were filtered from the data series, and compared to the visually defined precession (lithological couplets) and long-term and short-term eccentricity periodicities (Figure 4). The data-series in the depth domain was subsequently converted into a time series, based on the observed and interpreted dominant ~405 Kyr eccentricity cycle. Low-frequency band-pass filtering was then performed with Astrochron on the raw-data time series to remove long-term trends. High-precision extraction of dominant spectral components (Figure 5, Supplementary Figures 4, 5, 6), with long- and short-term cycles of eccentricity, obliquity and precession, were subsequently extracted with Taner bandpass filtering (Astrochron) and AnalySeries.

The MTM power spectrum estimates of the Ca-concentration in the depth domain show dominance of the >150 m spectral peak (Supplementary Figure 4A). Removal of this long-term trend by high band-pass filtering shows dominant spectral components at ~1, ~1.5, ~2.5, ~5.8 and ~24 m (Supplementary Figure 4B). Lithological observations and visually described changes in Ca-concentrations show a pronounced reduction in thickness of the observed lithological couplets, relative to the underlying Pliensbachian strata, in the upper *margaritatus* and complete *spinatum* zones (Figure 4). Individual couplets, however, continue to be spaced in the observed bundles (E^1) and super-bundles (E^2), and lack any evidence of periodic hiatuses. The reduced thickness of individual couplets, combined with the continued bundling, suggests an overall reduced sedimentation rate in this part of the Mochras core.

Individual MTM power spectra for the uppermost *raricostatum* to lower *margaritatus* and the upper *margaritatus* to lowermost *tenuicostatum* zones (Supplementary Figure 4C, 4D, respectively), show that dominant spectral components occur at different frequencies, but with equal internal ratios suggesting a ~40–60% reduction in sedimentation rate in the latest Pliensbachian and very earliest Toarcian (Supplementary Figure 7). The ~1 and ~0.6 m spectral components in these intervals directly reflect the observed primary sedimentary rhythms, recognized throughout the Pliensbachian of the Mochras core (Figure 4). The observed dominant spectral peaks directly reflect the visually ascribed individual lithological rhythms and bundles (E^1) and super-bundles (E^2) in carbonate predominance, likely representing precession and short- and long-term eccentricity. Using this interpretation, the sedimentary and geochemical time series of the Mochras core can be converted from depth to age. The resulting floating astronomical time scale for the Pliensbachian may also then be tuned to the proposed astronomical solutions for this period (e.g. Laskar et al., 2011), using radiometric tie points.

[5.4] ASTRONOMICAL CONSTRAINTS ON THE DURATION OF THE PLIENSBACHIAN STAGE AND AMMONITE ZONES

The base of the Pliensbachian is formally defined by a mudstone bed in the Pyritous Shale Member (Redcar Mudstone Formation) at Robin Hood's Bay, Yorkshire, UK, marked by the lowermost occurrence of the ammonite species *Bifericeras donovani*; with additional stratigraphical markers including a narrow reversed-polarity magnetozone (at the base of Si-Pl N) and a negative excursion in $\delta^{13}C$ (Hesselbo et al. 2000, Meister et al., 2006; Korte and Hesselbo, 2011). The Pliensbachian Stage is conventionally divided into the lower (Carixian) and upper (Domerian) substages and, at a higher resolution, into ammonite zones. Some authors, e.g. Page (2004), prefer to treat ammonite-based subdivisions as chronozones rather than biozones or zones but, given the absence of corroboration of their time significance, we treat them here as conventional biostratigraphical units. These are successions of sedimentary rock characterised by specific fossil assemblages, and defined to be (closely) approximate in depositional age and hence are characteristic of discrete time intervals.

The visual core observations and interpretations, combined with the spectral and multi-taper analyses of geochemical records, together with the precise biostratigraphical subdivision of the Mochras core, can be used to estimate the duration of Pliensbachian ammonite zones. The precision of the estimates obtained for ammonite zone durations depends on (1) the correct recognition of the dominant orbital signals, and (2) the uncertainty of the precise position of the stratigraphical base of an ammonite zone in the core. Here, we derive ammonite zone durations based on the observed 405 and ~100 Kyr forcing in the geochemical proxy-records. The stratigraphical occurrences of ammonite genera identified in the Upper Sinemurian to Lower Toarcian sections of the Mochras core, which are used to define the ammonite zones, is given in Supplementary Figure 7.

Ammonite zones at Mochras are recognized on the basis of occurrences of characteristic ammonite taxa within the core. Where ammonites are absent between the highest occurrence of one stratigraphically significant taxon and the lowest occurrence of another there is inevitably some uncertainty in the position of the biozone boundary (such range uncertainty for Mochras is indicated diagrammatically in Supplementary Figure 7 and Table 1). Given the above, resulting ammonite biozone durations are estimated at ~2.7 Myr (*jamesoni*), ~1.8 Myr (*ibex*), ~0.4 Myr (*davoei*), ~2.4 Myr (*margaritatus*) and ~1.4 Myr (*spinatum*), yielding a duration of the complete Pliensbachian Stage of ~8.7 Myr (Figure 4; Table 1).

The durations estimated here for the *jamesoni* and *ibex* zones are significantly longer than previous (minimum) estimates from the Belemnite Marl Member (Dorset) and the Ironstone Shale (Yorkshire) (van Buchem et al., 1994; Weedon & Jenkyns, 1999). The base and top of the Belemnite Marl Member (representing the base of the *jamesoni* ammonite zone and the top of the *ibex* ammonite zone in the Dorset outcrops) are marked by stratigraphic gaps (Hesselbo and Jenkyns, 1995; Weedon and Jenkyns, 1999), likely explaining their shorter estimated durations. Equally, the Ironstone Shale in Yorkshire shows strong evidence for condensation at the top of the *jamesoni* zone and within the *ibex* zone (Hesselbo and Jenkyns 1995, 1998; van Buchem and Knox, 1998).

The likely underestimated durations of Early Pliensbachian ammonite zones based on the Belemnite Marl Member sedimentary succession, are furthermore suggested by time series analyses of the Mochras % Ca data imposed onto the Belemnite Marl Member Early Pliensbachian time scale (Supplementary Figure 8), which shows spectral peaks that have no correspondence to dominant astronomical frequencies as known from the geological record and astronomical solutions (Supplementary Figure 8). The new duration estimated here for the *davoei* zone is similar to an earlier proposed value from Breggia Gorge in southern Switzerland, which was previously considered to be only 46% complete (Weedon, 1989). The latter was, however, based on the assumption that Jurassic ammonite zones were ~1 Myr in duration and that only 22 of the expected 48 precession cycles could be recognized (Weedon, 1989). Given the similar duration obtained for the *davoei* zone in the Mochras core, where no evidence for a hiatus, condensation, or non-deposition has been observed, we argue that the *davoei* zone in the Breggia Gorge section is probably complete. The estimated durations of the *margaritatus* and *spinatum* zones are significantly longer, respectively 0.7 and 0.6 Myr, compared to previous minimum estimates of Weedon (1989) and Weedon and Jenkyns (1999). Our estimated duration of ~3.8 Myr for the combined *margaritatus*–*spinatum* ammonite zones does, however, closely resemble previous estimates of ~3.96 Myr based on the assumed rate of change of Early Jurassic seawater $^{87}Sr/^{86}Sr$ (McArthur et al., 2000). This does, however, not infer that a linear change in $^{87}Sr/^{86}Sr$ likely occurred throughout the Pliensbachian Stage. A recent estimate on the duration of the Pliensbachian Stage and ammonite zones, with a stage duration of 8.1 Myr, does a-priori assume such linear change for all, but the *jamesoni* zones (McArthur et al., 2016). Such assumption is not necessarily correct, as the rate of change in the $^{87}Sr/^{86}Sr$ ratio of seawater can adjust on multiple time-scales in response to a change in global climate and associated continental (silicate) weathering rates, with a change in the flux of radiogenic $^{87}Sr/^{86}Sr$ to the global oceans, relative to the dominant long-term unradiogenic marine hydrothermal/basalt weathering Sr flux (see also section 5.7).

[5.5] TOWARDS AN ABSOLUTE TIME SCALE FOR THE EARLY JURASSIC HETTANGIAN TO PLIENSBACHIAN STAGES

Zircon U-Pb radiometric dating of the earliest Central Atlantic Magmatic Province (CAMP) flood basalts in eastern North America anchor the end-Triassic mass extinction at 201.56 ± 0.02 Ma, and volcaniclastic material in the Pucara Basin of Peru, indicates an age of 201.51 ± 0.15 Ma for the same event (Schoene et al., 2010; Blackburn et al., 2013; Wotzlaw et al., 2014). The age of the Triassic–Jurassic boundary is radiometrically constrained at 201.36 ± 0.17 Ma in the Pucara Basin (Schaltegger et al., 2008; Schoene et al., 2010; Wotzlaw et al., 2014) and astrochronologically constrained at 201.42 ± 0.02 Ma in the Newark/Hartford succession (Blackburn et al., 2013).

The duration of the Hettangian Stage has been previously estimated by cyclostratigraphy at >~1.29 Myr from the relatively incomplete marine Blue Lias Formation succession in Dorset and Devon, SW England, or at ~2.86 Myr based on an assumed constant linear Early Jurassic decrease in seawater $^{87}Sr/^{86}Sr$ ratios (Weedon and Jenkyns, 1999). More recent estimates for this stage suggest a duration of ~1.7–1.9 Myr, based on the astronomical interpretation of periodically occurring laminated black shales and systematic fluctuations in organic and inorganic geochemical proxy records in the relatively expanded Blue Lias Formation of Somerset, SW England (Ruhl et al., 2010; Hüsing et al., 2014). This duration is further supported by palaeomagnetic correlation to the Geomagnetic Polarity Time Scale (GPTS) of the Newark Basin, USA (Hüsing et al., 2014), and a 199.43 (±0.10) Ma $^{238}U/^{206}Pb$ age for the earliest Sinemurian in the Pucara Basin (Schaltegger et al., 2008; Guex et al., 2012). The duration of the Sinemurian Stage was relatively poorly constrained at ~7.62 Myr, based on assumed constant sedimentation rates and a linear decrease in $^{87}Sr/^{86}Sr$ (Weedon and Jenkyns, 1999).

Acknowledging recognized depositional gaps, earlier astrochronological analyses of the Pliensbachian in Dorset and Yorkshire (UK) and Breggia Gorge (Switzerland), suggested a minimum Pliensbachian Stage duration of 4.82 Myr (Weedon and Jenkyns, 1999); adjustment of these data to an assumed linear decrease in seawater $^{87}Sr/^{86}Sr$ of 0.000042 per Myr for the Belemnite Marl Member, lengthened this minimum duration of the Pliensbachian Stage to ~6.67 Myr (Weedon and Jenkyns, 1999). The $^{87}Sr/^{86}Sr$-based estimate of a ~3.96 Myr long, combined *margaritatus* and *spinatum* zone duration (McArthur et al., 2000), would suggest a much longer duration for the complete Pliensbachian Stage.

Absolute age constraints for the base Toarcian are relatively weak. U-Pb radiometric dating of Lower Jurassic volcanic ashes from the North American Cordillera, integrated with ammonite biochronology, gives ages of 185.7 +0.5/–0.6 Ma for the base of the *kunae* zone (which slightly predates the base of the European *margaritatus* ammonite zone), 184.1 +1.2/–1.6 Ma for the base of the *carlottense* zone (which is equivalent to the European *spinatum* ammonite zone), 183.6 +1.7/−1.1 Ma for the base of the *kanense* zone (which represents the Pliensbachian–Toarcian boundary and which is equivalent to the combined European *tenuicostatum* and *falciferum* ammonite zones), 182.0 +3.3/−1.8 Ma for the base of the *planulata* zone (which is equivalent to the European *bifrons* ammonite zone), and 181.4 ±1.2 Ma for the base of the *crassicosta* zone (which slightly post-dates the onset of the European *variabilis* ammonite zone) (Pálfy and Smith, 2000). Furthermore, a Re-Os isochron age based on several combined stratigraphical levels in the *falciferum* ammonite zone of the Jet Rock (Yorkshire, UK) suggests an age of 178 ±5 Ma for this time interval (Cohen et al., 2004). The methodological uncertainty on these earlier U-Pb and Re-Os radiometric dates is, however, relatively large, and much larger than one would ideally use for creating tie-points in a floating astrochronological time scale.

A bentonite at the base of the *falciferum*-equivalent ammonite zone (*levisoni*-equivalent ammonite subzone) in the Pucara Basin (Peru) was more recently radiometrically (U-Pb) dated at 183.22 ± 0.25 Myr (Sell et al., 2014). The relatively scarce ammonite occurrences in this section, combined with the bio- and chemostratigraphical uncertainty in correlation to the European realm (Guex et al., 2012), however, do also pose a problem for firmly anchoring the Early Toarcian zones to the numerical time scale. For now, these data, however, provide the basis for the least uncertain age estimate for this time interval, and are therefore used here to anchor the top of the Pliensbachian to the numerical time scale (Figure 6).

The *falciferum* ammonite zone follows the lowest Toarcian *tenuicostatum* zone in northwest Europe and the age-equivalent *polymorphum* zone in the Lusitanian Basin of Portugal. The duration of the *polymorphum* (and *tenuicostatum*) ammonite zone was astrochronologically constrained to 600–900 Kyr at Peniche in the Lusitanian Basin (Suan et al., 2008; Huang and Hesselbo, 2014; Ruebsam et al., 2014, 2015), to ~550 Kyr in the Lorraine Sub-Basin, France, and to a significantly shorter duration of 90–500 Kyr in the Sancerre core of the Paris Basin, France (Boulila et al., 2014). The large range in the Sancerre estimate primarily derived from biostratigraphical uncertainty on the exact position of the lowermost Toarcian in that core. Furthermore, the Lower Toarcian sedimentary record in the Lorraine Sub-Basin and especially also in the Paris Basin is marked by stratigraphical condensation, possibly in response to coeval sea-level change, which compromises the reliability of astrochronological constraints for this time interval, based on the sedimentary successions of these two depocentres (Boulila et al., 2014; Ruebsam et al., 2014, 2015). Assuming (1) the 183.22 ± 0.25 Myr radiometric age for the base of the *falciferum* zone in the Pucara Basin, Peru (Sell et al., 2014), (2) a synchronous age for the *tenuicostatum*–*falciferum* zonal boundary in north-western Europe, the *kanense*–*planulata* zonal boundary in South America, and the *polymorphum*–*levisoni* zonal boundary in the Lusitanian Basin, and (3) a ~600 ± 150 Kyr duration for the *polymorphum* (*tenuicostatum*) zone, a 183.8 ± 0.4 Ma age can, tentatively, be assigned to the base of the Toarcian (Figure 6).

The duration of the combined Toarcian *tenuicostatum* and *falciferum* zones is currently much debated, with estimates ranging from ~1.9 Myr (Suan et al., 2008), to ~1.4 or 2.4 Myr (Kemp et al., 2011), ~2.5 Myr (Huang and Hesselbo, 2014), ~1.54−1.71 Myr (Boulila et al., 2014) and >1.8 Myr (Ruebsam et al., 2014, 2015), depending primarily on differences in the precession versus obliquity versus eccentricity interpretation of astronomically forced steps in the Early Toarcian carbon-isotope ($\delta^{13}C$) and other geochemical proxy records. Seawater $^{87}Sr/^{86}Sr$-based estimates for this time interval suggested a duration of ~1.694 Myr (McArthur et al., 2000), but this figure is problematic because of large-scale tectono-climatic events over this time interval that may have significantly varied Sr fluxes from both mantle and continental sources, and because of a distinctly European epicontinental data bias.

The radiometrically constrained age of 199.43 ± 0.10 Ma for the base-Sinemurian and the 183.8 ± 0.4 Ma age assigned here for the base Toarcian, suggest a ~15.6 Myr duration for the combined Sinemurian and Pliensbachian Stages (Schaltegger, 2008; Schoene, et al., 2010; Guex et al., 2012). In conjunction with the ~8.7 Myr duration of the Pliensbachian Stage estimated here, we suggest that the Sinemurian Stage was ~700 Kyr shorter than previously estimated and had a duration of 6.9 ± 0.4 Myr, with a 192.5 ± 0.4 Ma age for the base-Pliensbachian (the ± 0.4 Ma uncertainty derives from the combined radiometric and astrochronological uncertainty on the age of Early Toarcian ash-beds in Peru and the duration of the Early Toarcian *tenuicostatum* zone, respectively) (Figure 6; Table 1).

An astronomically calibrated absolute time scale has been constructed successfully for the Neogene and part of the Paleogene (Hilgen et al., 2014). Astronomical solutions for the geological past, however, become increasingly uncertain, especially before ~50 Ma, due to multiple secular resonances in the inner solar system, and in particular with respect to the θ argument ($\theta = (s_4 - s_3) - 2(g_4 - g_3)$, where g_3 and g_4 are related to precession of the perihelion and s_3 and s_4 are related to precession of the node of Earth and Mars) (Laskar et al., 2004, 2011). The 405 Kyr eccentricity cycle, related to the ($g_2 - g_5$) argument, which reflects the motions of the orbital perihelia of (gravitational pull between) Jupiter and Venus, however, remained relatively stable over the past 250 Myr (Laskar et al., 2004). Different solutions for the 405 Kyr periodicity show a maximum deviation of 2π over 250 Myr, corresponding to a maximum error of <350 Kyr at 200 Ma (Laskar et al., 2004, 2011). The 405 Kyr eccentricity solution, combined with precise radiometric anchor points, can therefore be used as a target curve for the astronomical tuning of floating astronomical time scales, potentially even back into the Mesozoic.

Precise radiometric and astrochronological age constraints for the base of the Hettangian and the base of the Sinemurian potentially allow the Hettangian floating astronomical time scales to be accurately anchored to the stable 405 Kyr eccentricity solution (La2010d) of Laskar et al. (2011) (Figure 6). However, given the radiometric and astrochronological uncertainties for the age of the base-Toarcian, and with that the age of the base-Pliensbachian, we are presently unable to uniquely anchor the Pliensbachian floating astronomical time scale obtained here to the absolute (numerical) time scale and 405 Kyr astronomical solution of Laskar et al. (2011). We therefore propose 3 different models, Options A, B and C (Figure 6). Option-A represents the solution with the youngest base Jurassic and oldest base Toarcian, Option-B represents the solution with the oldest base Jurassic and youngest base Toarcian, and Option-C represents the intermediate case (Figure 6). Importantly, different solutions for the 405 Kyr periodicity show a maximum deviation of <350 Kyr in the Early Jurassic (Laskar et al., 2004), which adds additional uncertainty to this tuning. Consequently, it is currently not possible to assign with confidence particular observed peaks in the proxy records to either the maxima or minima of the 405 Kyr eccentricity cycle.

Astronomically forced changes in bed thickness in the Early Jurassic pelagic chert sequences from the Panthalassic Ocean (Inuyama, Japan) show also dominant precession and short and long eccentricity periodicities (Ikeda and Hori, 2014; Ikeda and Tada, 2014). The end-Triassic mass extinction event and the Pliensbachian–Toarcian boundary are well constrained in these successions, with radiolarian biostratigraphy allowing biostratigraphical correlation with North American and European ammonite zones (Hori, 1990, 1992, 1997). Interestingly, the number of recognised ~405 Kyr eccentricity cycles across the Hettangian to Pliensbachian stages in the Inuyama chert sequence directly match the number of 405 kyr eccentricity cycles suggested here for this time-period (Option C, Figure 6). Although the Hettangian–Sinemurian and Sinemurian–Pliensbachian boundary are biostratigraphically not very well constrained in the Inuyama chert sequences, Early Jurassic high-resolution astrochronological correlation may be possible between the pelagic and the continental margin realms of the Panthalassa Ocean and the western Tethys, respectively.

[5.6] RATE AND DURATION OF PLIENSBACHIAN CLIMATIC AND GLOBAL CARBON-CYCLE CHANGE

The Early Jurassic was marked by large perturbations in global geochemical cycles, palaeoclimate and the palaeoenvironment, especially at the Triassic–Jurassic transition and in the Early Toarcian (Hesselbo et al., 2002; Jenkyns, 2003, 2010; Korte et al., 2009; Korte and Hesselbo, 2011; Ruhl et al., 2011; Suan et al., 2011; Ullmann et al., 2014; Brazier et al., 2015; Krencker et al., 2015; Al-Suwaidi et al., 2016; and many others).

Recent studies show that the Pliensbachian Stage was also marked by major perturbations in the global carbon cycle and possibly (global) climate. The Early Pliensbachian *jamesoni* zone is marked by a negative shift in $\delta^{13}C$ (of 2–4‰) in marine calcite and organic matter (Jenkyns et al., 2002; van de Schootbrugge et al., 2005; Woodfine et al., 2008; Korte and Hesselbo, 2011; Armendariz et al., 2012; Franceschi et al, 2014; Korte et al., 2015). This shift is also seen in the $\delta^{13}C$ of wood, reflecting global atmospheric change and a rearrangement of the global exogenic carbon cycle, possibly by the release of isotopically depleted carbon into the ocean-atmosphere system (Korte and Hesselbo, 2011). The Late Pliensbachian *margaritatus* zone (*subnodosus* and *gibbosus* subzones) is further marked by a distinct positive shift in $\delta^{13}C$ of marine and terrestrial organic matter, marine calcite and wood (Jenkyns and Clayton, 1986; van de Schootbrugge et al., 2005; Suan et al., 2010; Korte and Hesselbo, 2011; Silva et al., 2011), possibly linked to enhanced carbon burial under favourable marine redox conditions (Hesselbo and Jenkyns, 1995; Suan et al., 2010; Korte and Hesselbo, 2011; Silva et al., 2011; Silva and Duarte, 2015). Possible changes in Pliensbachian atmospheric $p\mathrm{CO}_2$, based on carbon-isotope and leaf stomatal index data, may have affected regional and/or global temperatures (Suan et al., 2008, 2010; Korte and Hesselbo, 2011; Armendariz et al., 2013; Steinthorsdottir and Vajda, 2013; Silva and Duarte, 2015).

The tuned astrochronological time scale for the Pliensbachian presented here, suggests that the Early Pliensbachian negative CIE had a duration of ~2 Myr, possibly linked to a recurrent phase of CAMP magmatism (see also section 5.7; Figures 7, 8). The Late Pliensbachian (upper *margaritatus* zone) $\delta^{13}C$ positive excursion coincided with significant sea level fluctuations, possibly in synchrony with decreasing shallow-marine benthic temperatures (Hesselbo et al., 2008; Korte and Hesselbo, 2011). The Late Pliensbachian (upper *margaritatus* zone) positive carbon-isotope excursion has an estimated duration of ~0.6 Myr (Figure 7).

[5.7] CAMP VOLCANISM AND THE EARLY JURASSIC STEPPED $^{87}Sr/^{86}Sr$ RECORD

Seawater $^{87}Sr/^{86}Sr$ ratios and strontium fluxes to the oceans are controlled by hydrothermal circulation at mid-ocean ridges and other types of basalt-seawater interaction, the continental weathering of silicates, and the dissolution of carbonates, while the fluxes out of the ocean are primarily regulated by carbonate burial (Burke et al., 1982; Elderfield, 1986; Jones et al. 1994a, b; Steuber and Veizer, 2002; Allègre et al., 2010; Krabbenhöft et al., 2010; Ullmann et al., 2013). Changes in seawater $^{87}Sr/^{86}Sr$ ratios can therefore be explained by the change in the relative importance of continental weathering, or a change in the Sr-isotopic composition of the weathering flux, and hydrothermal inputs of Sr into the oceans. The global unradiogenic strontium flux from hydrothermal venting and weathering of fresh ocean-crust along mid-ocean ridges and around island arcs, is probably relatively stable over shorter time scales, but may have varied on tectonic time scales, with changes in the rate of ocean-crust formation along mid-ocean ridge systems and changes in the global extent of spreading ridges and ocean island arcs (Allègre et al., 2010; Van der Meer et al., 2014). The global unradiogenic Sr-flux may also have varied on long (>Myr) Milankovitch periodicities, possibly in response to eustatic sea-level change and changing mid-ocean ridge spreading rates (Cohen and Coe, 2007; Crowley et al., 2015).

In the Early Jurassic, seawater ^{87}Sr/^{86}Sr ratios show an overall decrease over ~20 Myr towards unradiogenic values, from ~0.70775 to ~0.70705 (Jones et al., 1994a; Cohen and Coe, 2007). Proto-Atlantic rifting at this time initiated on the continents, but continued throughout the Jurassic as mid-ocean ridge activity. Increased mid-ocean ridge spreading rates and/or the increased global extent of mid-ocean spreading ridges, combined with the possible increased formation of island arcs, may have provided an enhanced unradiogenic strontium flux to the global oceans (Van der Meer et al., 2014), leading to the observed steady decrease in Early Jurassic seawater ^{87}Sr/^{86}Sr up to the Pliensbachian–Toarcian boundary (Jones et al., 1994a, b; Jenkyns et al., 2002). A decline in seawater ^{87}Sr/^{86}Sr may alternatively be explained by a decrease in the overall continental weathering flux. However, in the absence of a major orogeny in the Early and Middle Jurassic, the ^{87}Sr/^{86}Sr ratio of the global weathering flux probably remained relatively stable (Jones et al., 1994b). The changing style of biomineralization shown by the evolutionary adoption of calcite in Jurassic calcifying organisms, and increasing pelagic calcite production, probably did not play a major role in the observed change in seawater chemistry because seawater Sr/Ca ratios changed in parallel with Sr-isotope ratios, indicating a likely common weathering and/or tectonic origin for both (Ullmann et al., 2013).

The base Jurassic Hettangian Stage, however, contrasts in being marked by a ~2 Myr plateau, with relatively stable ^{87}Sr/^{86}Sr ratios of ~0.70775 (Cohen and Coe, 2007), suggesting the balancing of the unradiogenic Sr flux from basalt-seawater interaction, by supply of radiogenic Sr from the weathering of old continental crust. This period was also marked by major flood-basalt emplacement, with the onset of CAMP volcanism in the latest Triassic, coeval with the end-Triassic mass extinction, at ~201.4 Ma. Its onset preceded the Triassic–Jurassic boundary, defined by the first occurrence of the Jurassic ammonite species *Psiloceras spelae (tirolicum)* (and *Psiloceras spelea (spelae)*), by 100–200 Kyr (Marzoli et al., 1999; Hesselbo et al., 2002; Deenen et al., 2010, 2011; Ruhl et al., 2010; Schoene et al., 2010; Whiteside et al., 2010; Ruhl and Kürschner, 2011; Blackburn et al., 2013; von Hillebrandt et al., 2013; Dal Corso et al., 2014; Hüsing et al., 2014). Astrochronological and radiometric dating constrain emplacement of the major CAMP flood-basalt pulses in the eastern North American Newark, Culpeper, Hartford and Deerfield basins, the Canadian Fundy Basin, the Algarve in Portugal, the Moroccan Argana Basin and the Moroccan High Atlas Mountains, within a relatively short period of time, possibly within 1 Myr after its onset (Olsen et al., 2003; Deenen et al., 2010, 2011; Marzoli et al., 2011; Fernandes et al., 2014). The chemical weathering of juvenile basaltic rocks from CAMP is, however, unlikely to have been directly responsible for stabilizing the Hettangian seawater ^{87}Sr/^{86}Sr signal, because Sr-isotope values of fresh Large Igneous Province basalts (with values of 0.704–0.706), are much less radiogenic than ambient Early Jurassic seawater (Cohen and Coe, 2007).

The release of volcanogenic CO_2 and biogenic and thermogenic methane from sea-floor clathrates and subsurface organic-rich facies following CAMP flood-basalt emplacement and dyke and sill intrusions (Hesselbo et al., 2002; Korte et al. 2009; Ruhl et al., 2011; Schaller et al., 2011), combined with enhanced greenhouse-gas-induced elevated hydrological cycling (Ruhl et al., 2011; Bonis and Kürschner, 2012), may have enhanced the global weathering of crustal silicates, carbonates and evaporates, and the consequent flux of more radiogenic Sr to the global oceans (Jones and Jenkyns, 2001; Cohen and Coe, 2007).

CAMP-attributed flood-basalt emplacement and dyke and sill intrusions may, however, have continued for millions of years into the Early Jurassic, with a late phase of CAMP magmatism dated as of Early–Middle Pliensbachian age by ^{40}Ar/^{39}Ar (Baksi and Archibald, 1997; Deckart et al., 1997; Marzoli et al., 1999; Hames et al., 2000; Knight et al., 2004; Marzoli et al., 2004; Beutel et al., 2005; Verati et al., 2007; Nomade et al., 2007; Jourdan et al., 2009; Marzoli et al., 2011).

Sinemurian and Pliensbachian seawater ^{87}Sr/^{86}Sr ratios are often considered to show a relatively constant decline towards the Early Toarcian minimum (with values down to ~0.70705), at which point relatively enhanced continental silicate weathering in response to Early Toarcian Karoo-Ferrar volcanism induced a rapid reversal of this trend to renewed relatively elevated seawater ^{87}Sr/^{86}Sr values (Cohen and Coe, 2007). However, this supposed constant rate of decline in seawater ^{87}Sr/^{86}Sr may be an artefact of the assumption of equal duration ammonite (sub-)zones. Conversion of the Pliensbachian seawater ^{87}Sr/^{86}Sr record of Jones et al. (1994) and Jenkyns et al. (2002) to the Pliensbachian astrochronological time scale proposed here shows 4 distinct phases of enhanced decline in seawater ^{87}Sr/^{86}Sr superimposed on the Early Jurassic long-term fall in values, with a potential periodicity of ~2.4 Myr (Figure 8). The veracity of the observed changes in this trend relies on the accuracy of the positioning of the base of individual (sub)zones in both the outcrops and especially the Mochras core, and their precision as time markers. Although ammonite stratigraphy in cores might generally be less precise compared to that in outcrops, where fossil occurrences can be traced laterally, along geographically extensive bedding-planes, the precision of the assigned bases of (sub)zones in the Mochras core is relatively good (Table 1; Supplementary Figure 7) and was further refined by the identification and correlation of recognized foraminiferal zones (Copestake and Johnson, 2013).

Phases of enhanced decline in seawater ^{87}Sr/^{86}Sr may reflect periodic, long-term (>Myr) Milankovitch-forced, decreases in global continental weathering rates, with a diminished flux of radiogenic Sr. Interestingly, the onset of the Pliensbachian Stage is also marked by a plateau in seawater ^{87}Sr/^{86}Sr ratios, with stable values for ~2 Myr, closely resembling the pattern in the base Jurassic Hettangian Stage during the major phase of CAMP emplacement (Figure 8). This plateau in ^{87}Sr/^{86}Sr temporally coincides with a late phase of CAMP magmatism, with surface flood-basalt and subsurface sill emplacement in the eastern USA, Brazil and Guinea (Figure 8; Deckart et al., 1997; Marzoli et al., 1999; Nomade et al., 2007). The onset and duration of this plateau in ^{87}Sr/^{86}Sr also directly coincides with the earliest Pliensbachian (*jamesoni* zone) negative CIE, similar in magnitude (~2–4‰) and duration to the earliest Jurassic (Hettangian) long-term 'main' negative CIE (Figure 8; Hesselbo et al., 2002; Korte et al., 2009; Ruhl et al., 2010; Bartolini et al. 2012). The observed Early Pliensbachian plateau in ^{87}Sr/^{86}Sr ratios may, therefore, reflect a second Early Jurassic phase of CAMP-induced climatic and carbon-cycle perturbation that, as inferred for the Hettangian, also led to increased global weathering and an enhanced radiogenic Sr flux from the continents to the oceans. The inference of the Early Pliensbachian plateau in ^{87}Sr/^{86}Sr ratios depends on (1) the correct biostratigraphical correlation between the ^{87}Sr/^{86}Sr record, as measured in outcrops, and the Mochras core-based Early Pliensbachian astrochronology and (2) the correctness of the interpreted unequal duration of Pliensbachian zones, specifically the Early Pliensbachian (*jamesoni*) (sub)zones. If all the above is correct, then one may conclude that subsequent phases of CAMP volcanism led to elevated atmospheric pCO$_2$ and increased global continental (silicate) weathering rates that balanced the dominant long-term unradiogenic marine hydrothermal/basalt weathering Sr flux and resulted in the observed (Hettangian and Early Pliensbachian) ~2 Myr plateaus in the Early Jurassic ^{87}Sr/^{86}Sr record.

[6] CONCLUSIONS

Periodic alternations in lithology and geochemical palaeoenvironmental proxies through the expanded and biostratigraphically complete Pliensbachian of the Mochras core (Llanbedr/ Mochras Farm borehole, Wales, UK) reflect Milankovitch forcing, predominantly at precession and short- and long-eccentricity periodicities. The duration of Pliensbachian ammonite zones is cyclostratigraphically constrained at ~2.7 Myr (*jamesoni*), ~1.8 Myr (*ibex*), ~0.4 Myr (*davoei*), ~2.4 Myr (*margaritatus*) and ~1.4 Myr (*spinatum*), with a combined duration of ~8.7 Myr for the complete Pliensbachian Stage. These figures, combined with radiometric and astrochronological constraints on the age of the base of the Toarcian, suggest a Sinemurian–Pliensbachian boundary age of 192.5 ± 0.4 Ma.

Calibration of the floating astronomical time scale for the Pliensbachian to the 405 Kyr eccentricity solution (La2010d) gives absolute ages for the Pliensbachian ammonite biozone boundaries and the base Pliensbachian (*jamesoni* zone) global exogenic carbon cycle perturbation. The negative excursion in δ^{13}C in the base Pliensbachian has a 2–4‰ amplitude and an astrochronologically defined duration of ~2 Myr. The Late Pliensbachian (upper *margaritatus* zone) global positive excursion in δ^{13}C, which coincides with a seawater cool phase in the European realm as revealed by δ^{18}O from macrofossil calcite, has a duration of ~0.6 Myr.

Calibration of the Pliensbachian ^{87}Sr/^{86}Sr record to the obtained astrochronological age model suggests modulation with a ~2.4 Myr periodicity of the Pliensbachian long-term decreasing trend to less radiogenic values. The Pliensbachian ^{87}Sr/^{86}Sr record also shows a stable plateau in the Early Pliensbachian *jamesoni* zone, coinciding with the observed δ^{13}C negative shift of 2–4‰, and possibly reflecting elevated continental weathering, with a relatively increased flux of radiogenic ^{87}Sr/^{86}Sr to the global oceans, in response to a late phase of enhanced global continental (silicate) weathering induced by CAMP volcanism.

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FIGURE CAPTIONS

FIGURE 1 Early Jurassic palaeogeography showing the Mochras (Cardigan Bay Basin) and Staithes (Cleveland Basin) localities (red stars) at the northwestern extremity of the Tethys Ocean. The figure is modified after Dera et al. (2011) and Korte et al. (2015).

FIGURE 2 The relative thickness of the Lower Jurassic stages in the Mochras core and outcrops and boreholes in the UK, France and Portugal (Ivimey-Cook, 1971; Cope et al., 1980; Whittaker and Green, 1983; Lorenz and Gely, 1994; Ainsworth and Riley, 2010; Brigaud et al., 2014; Mattioli et al., 2013; and references therein). The 'T', 'HS' and 'PL' numbers refer to the stratigraphical columns in Cope et al. (1980).

FIGURE 3 Early Pliensbachian (*jamesoni* zone) lithology and XRF-derived geochemical data (calcium, titanium, iron, rubidium) showing sub-metre scale fluctuations. Calcium concentrations are superimposed on stacked core photographs showing a clear association with lithology/rock-colour. Four to five carbonate beds are grouped into bundles (E^{-1}) and super-bundles (E^{-2}), hypothetically representing short (~100 Kyr) and long (~405 Kyr) eccentricity. High values for Ti, Fe and Rb correlate closely with periodically low concentrations of Ca, suggesting carbonate dilution of other sedimentary components.

FIGURE 4 XRF-derived calcium and titanium record spanning the entire Pliensbachian Stage (from the Late Sinemurian *raricostatum* zone into the Early Toarcian *tenuicostatum* zone). Mochras core biostratigraphy following Ivimey-Cook (1971), Page (2003), and Copestake and Johnson (2013). The palaeomagnetic field directions from numerous outcrop studies are correlated to the Mochras core biostratigraphical record following the Geological Time Scale (GTS) 2012 (Gradstein et al., 2012). Ca content, superimposed on the stacked core photograph record, shows short-, intermediate- and long-periodicity fluctuations, with (A) the complete core, (B) part of the Late Sinemurian *raricostatum* and complete Early Pliensbachian *jamesoni* ammonite zones, (C) the Pliensbachian *ibex* and *davoei* ammonite zones and (D) the Upper Pliensbachian *margaritatus* and *spinatum* ammonite zones. The short- and intermediate-periodicity band-pass filters reflect dominant spectral peaks in the depth-domain (Supplementary Figure 2; see also section 5.3), suggesting a combined duration of ~8.7 Myr for the complete Pliensbachian Stage (see Supplementary Figure 4). Grey arrows show intervals with possibly dominant obliquity forcing.

FIGURE 5 Multi-taper (MTM; 3π) spectral and wavelet analyses of the XRF elemental (Fe) time series obtained using the Astrochron toolkit (R (3.1.2) Package for astrochronology, version 0.3.1; Meyers, 2014), with robust red noise models (Mann and Lees, 1996). The elemental Fe record was first re-sampled to uniform sample spacing using linear interpolation. Initial spectral analysis was performed with AnalySeries on a detrended data-series (with low band-pass filtering to remove >150 m periodicities). Dominant spectral components (Supplementary Figures 2, 3) were filtered from the data series and compared to the visually defined precession and short- and long-eccentricity periodicities (Figure 4). The elemental Fe record in the depth domain was subsequently converted to the time domain following the observed 405 Kyr eccentricity cycles. The multi-taper (MTM; 3π) spectral and wavelet analyses of the obtained elemental (Fe) time series show dominant and significant peaks at precession (~21 and ~26 Kyr), obliquity (~41 Kyr), short-period eccentricity (~100 and ~134 Kyr), long-period eccentricity (~405 Kyr) and also long-term periodicity (~640 and 2500 Kyr).

FIGURE 6 Calibration of the obtained Pliensbachian 405-Kyr eccentricity series to the astronomical solution (La2010d) of Laskar et al. (2011) allows for 3 different options

(A, B and C) due to the ~250 Kyr uncertainty in U-Pb radiometric dating of the base *falciferum* zone in the Pucara Basin in Peru and the ~200 Kyr uncertainty in the astrochronologically estimated duration of the base Toarcian *polymorphum* (*tenuicostatum*) zone in the Lusitanian Basin, Portugal (see also section 7.2). Radiometric and astrochronological constraints on the age of the base-Hettangian (Triassic–Jurassic) and base-Sinemurian Stage boundaries and the duration of the Hettangian Stage and the *polymorphum* zone are from Kent and Olsen (2008), Schaltegger et al. (2008), Suan et al. (2008), Ruhl et al. (2010), Schoene et al. (2010), Guex et al. (2012), Blackburn et al. (2013), Huang and Hesselbo (2014), Hüsing et al. (2014) and Sell et al. (2014). Orange bars present the reported radiometric uncertainty. The Hettangian palaeomagnetic record is from Kent and Olsen (2008) and Hüsing et al. (2014). The Pliensbachian palaeomagnetic record is from the Geological Time Scale (GTS) 2012 (Gradstein et al., 2012).

FIGURE 7 The Pliensbachian $\delta^{13}C$ record of marine calcite and wood from UK outcrops (Jenkyns et al., 2002; Korte and Hesselbo, 2011) and $\delta^{13}C$ of bulk organic matter ($\delta^{13}C_{TOC}$) from Staithes (this study; Yorkshire, UK (locality described in Korte and Hesselbo, 2011)), calibrated to the Pliensbachian floating astronomical time scale, using zone boundaries as tie-points and linear-interpolation within a zone.

FIGURE 8 The Pliensbachian seawater $^{87}Sr/^{86}Sr$ record calibrated against the newly derived floating astrochronological time scale, using subzone boundaries in outcrops (that yielded $^{87}Sr/^{86}Sr$ data) and the Mochras core as tie-points, and linear interpolation within subzones. The time-calibrated $^{87}Sr/^{86}Sr$ record shows periodically enhanced decline (grey arrows) superimposed on a long-term decrease from ~0.70745 to ~0.70710. The base of the Pliensbachian is, furthermore, marked by a plateau in $^{87}Sr/^{86}Sr$ (blue arrows), coinciding with a global carbon-cycle perturbation and recurrent Central Atlantic Magmatic Province (CAMP) volcanism. Early Jurassic $^{87}Sr/^{86}Sr$ values are from Jones et al. (1994b) and Jenkyns et al. (2002) (data were normalized to a value of the NBS987 standard of 0.710250, with $24*10^{-6}$ added to the published data of Jones et al. (1994b), which was normalized to a different standard). The Pliensbachian $\delta^{13}C$ record is from Jenkyns et al. (2002) and Korte and Hesselbo (2011). Upper Triassic/Lower Jurassic radiometric dating of CAMP magmatism comes from Baksi and Archibald (1997), Deckart et al. (1997), Marzoli et al. (1999), Hames et al. (2000), Marzoli et al. (2004), Knight et al. (2004), Beutel et al. (2005), Verati et al. (2007), Nomade et al. (2007), Jourdan et al. (2009), Marzoli et al. (2011) and Blackburn et al. (2013). The dark grey area in the upper graph shows the cumulative probability of CAMP magmatism through time, following uncertainties on U-Pb and the recalculated $^{40}Ar/^{39}Ar$ radiometric dates of individual basalt formations.

TABLE 1 Absolute age, uncertainty and duration estimates for the (base of) the Early Jurassic stages (Hettangian, Sinumurian, Pliensbachian and Toarcian) and the Hettangian and Pliensbachian zones. Basal-age and durations based on Kent and Olsen (2008), Schaltegger et al. (2008), Suan et al. (2008), Ruhl et al. (2010), Schoene et al. (2010), Guex et al. (2012), Blackburn et al. (2013), Boulila et al., 2014; Huang and Hesselbo (2014), Hüsing et al. (2014), Ruebsam et al., 2014 and Sell et al. (2014).

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FIGURE 1

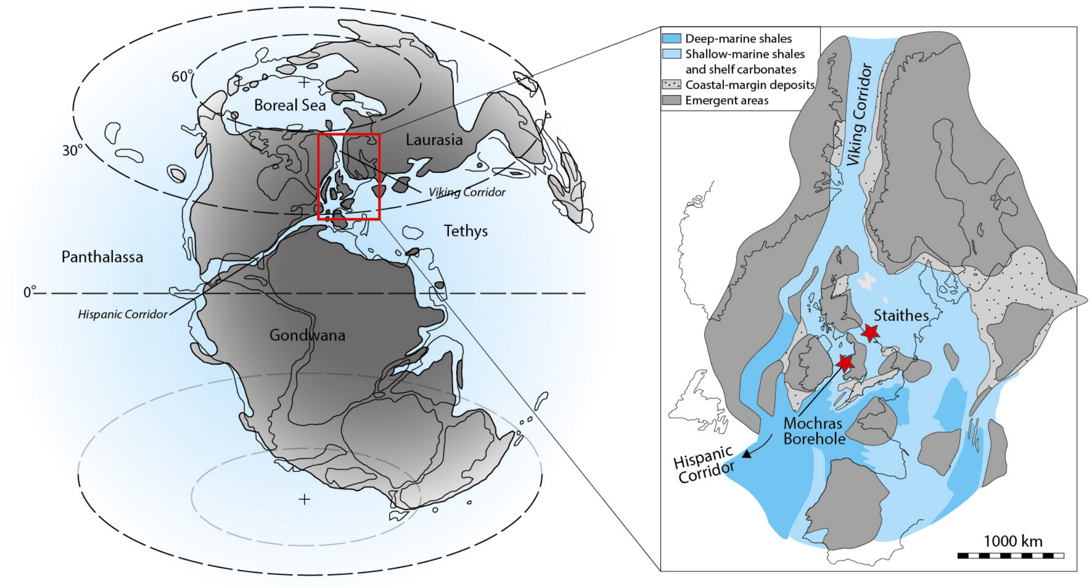

60°
30°
0°
Boreal Sea
Laurasia
Viking Corridor
Tethys
Panthalassa
Hispanic Corridor
Gondwana
Deep-marine shales
Shallow-marine shales and shelf carbonates
Coastal-margin deposits
Emergent areas
Viking Corridor
Staithes
Mochras Borehole
Hispanic Corridor
1000 km

FIGURE 2

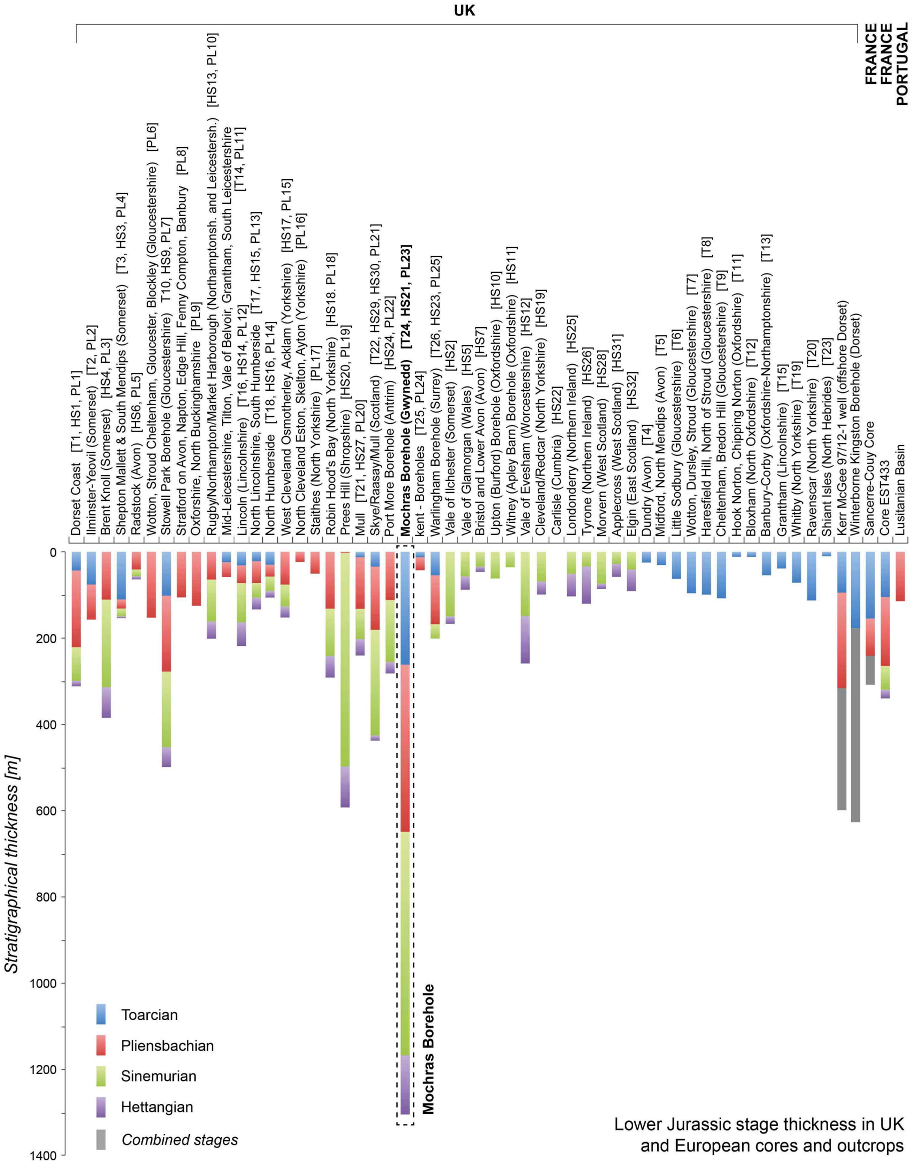

UK
FRANCE
FRANCE
PORTUGAL
Dorset Coast [T1, HS1, PL1]
Ilminster-Yeovil (Somerset) [T2, PL2]
Brent Knoll (Somerset) [HS4, PL3]
Shepton Mallett & South Mendips (Somerset) [T3, HS3, PL4]
Radstock (Avon) [HS6, PL5]
Wotton, Stroud Cheltenham, Gloucester, Blockley (Gloucestershire) [PL6]
Stowell Park Borehole (Gloucestershire) T10, HS9, PL7]
Stratford on Avon, Napton, Edge Hill, Fenny Compton, Banbury [PL8]
Oxforshire, North Buckinghamshire [PL9]
Rugby/Northampton/Market Harborough (Northamptonsh. and Leicestersh.) [HS13, PL10]
Mid-Leicestershire, Tilton, Vale of Belvoir, Grantham, South Leicestershire [T14, PL11]
Lincoln (Lincolnshire) [T16, HS14, PL12]
North Lincolnshire, South Humberside [T17, HS15, PL13]
North Humberside [T18, HS16, PL14]
West Cleveland Osmotherley, Acklam (Yorkshire) [HS17, PL15]
North Cleveland Eston, Skelton, Ayton (Yorkshire) [PL16]
Staithes (North Yorkshire) [PL17]
Robin Hood's Bay (North Yorkshire) [HS18. PL18]
Prees Hill (Shropshire) [HS20, PL19]
Mull [T21, HS27, PL20]
Skye/Raasay/Mull (Scotland) [T22, HS29, HS30, PL21]
Port More Borehole (Antrim) [HS24, PL22]
Mochras Borehole (Gwynedd) [T24, HS21, PL23]
kent - Boreholes [T25, PL24]
Warlingham Borehole (Surrey) [T26, HS23, PL25]
Vale of Ilchester (Somerset) [HS2]
Vale of Glamorgan (Wales) [HS5]
Bristol and Lower Avon (Avon) [HS7]
Upton (Burford) Borehole (Oxfordshire) [HS10]
Witney (Apley Barn) Borehole (Oxfordshire) [HS11]
Vale of Evesham (Worcestershire) [HS12]
Cleveland/Redcar (North Yorkshire) [HS19]
Carlisle (Cumbria) [HS22]
Londonderry (Northern Ireland) [HS25]
Tyrone (Northern Ireland) [HS26]
Morvern (West Scotland) [HS28]
Applecross (West Scotland) [HS31]
Elgin (East Scotland) [HS32]
Dundry (Avon) [T4]
Midford, North Mendips (Avon) [T5]
Little Sodbury (Gloucestershire) [T6]
Wotton, Dursley, Stroud (Gloucestershire) [T7]
Haresfield Hill, North of Stroud (Gloucestershire) [T8]
Cheltenham, Bredon Hill (Gloucestershire) [T9]
Hook Norton, Chipping Norton (Oxfordshire) [T11]
Bloxham (North Oxfordshire) [T12]
Banbury-Corby (Oxfordshire-Northamptonshire) [T13]
Grantham (Lincolnshire) [T15]
Whitby (North Yorkshire) [T19]
Ravenscar (North Yorkshire) [T20]
Shiant Isles (North Hebrides) [T23]
Kerr McGee 97/12-1 well (offshore Dorset)
Winterborne Kingston Borehole (Dorset)
Sancerre-Couy Core
Core EST433
Lusitanian Basin
Stratigraphical thickness [m]
0
200
400
600
800
1000
1200
1400
Toarcian
Pliensbachian
Sinemurian
Hettangian
Combined stages
Mochras Borehole
Lower Jurassic stage thickness in UK and European cores and outcrops

FIGURE 3

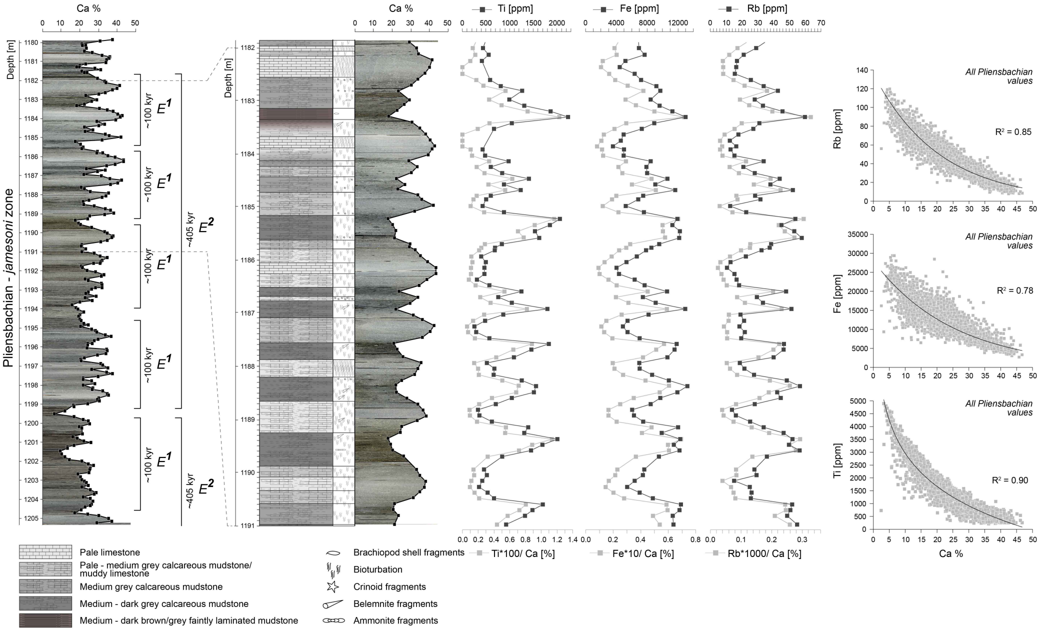
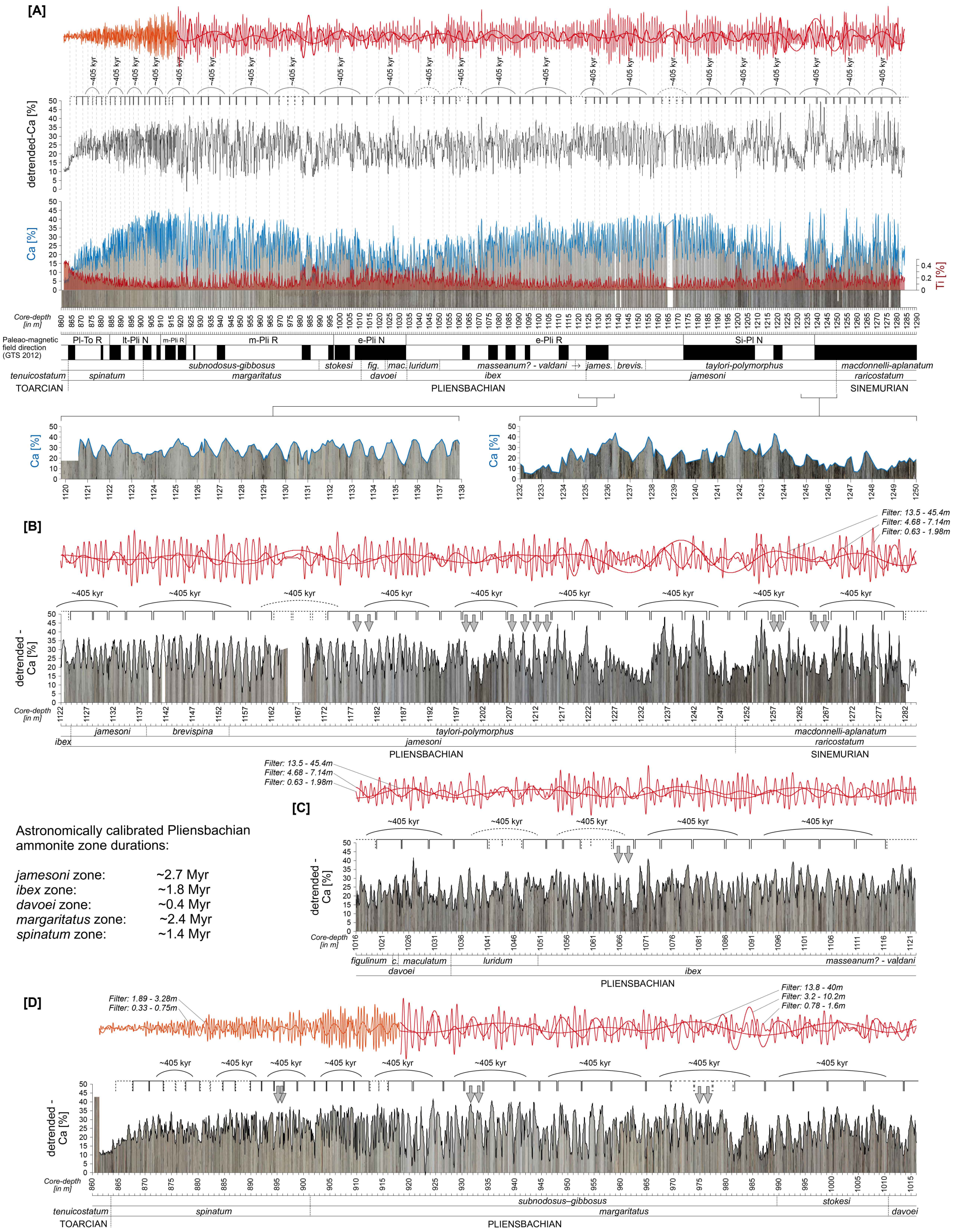

Ca %
Depth [m]
Pliensbachian - jamesoni zone
~100 kyr
E^1
~405 kyr
E^2
Ti [ppm]
Fe [ppm]
Rb [ppm]
Ti*100/ Ca [%]
Fe*10/ Ca [%]
Rb*1000/ Ca [%]
All Pliensbachian values
Rb [ppm]
R² = 0.85
Fe [ppm]
R² = 0.78
Ti [ppm]
R² = 0.90
Ca %
Pale limestone
Pale - medium grey calcareous mudstone/ muddy limestone
Medium grey calcareous mudstone
Medium - dark grey calcareous mudstone
Medium - dark brown/grey faintly laminated mudstone
Brachiopod shell fragments
Bioturbation
Crinoid fragments
Belemnite fragments
Ammonite fragments

FIGURE 4



Astronomically calibrated Pliensbachian ammonite zone durations:

jamesoni zone:	~2.7 Myr
ibex zone:	~1.8 Myr
davoei zone:	~0.4 Myr
margaritatus zone:	~2.4 Myr
spinatum zone:	~1.4 Myr

FIGURE 5

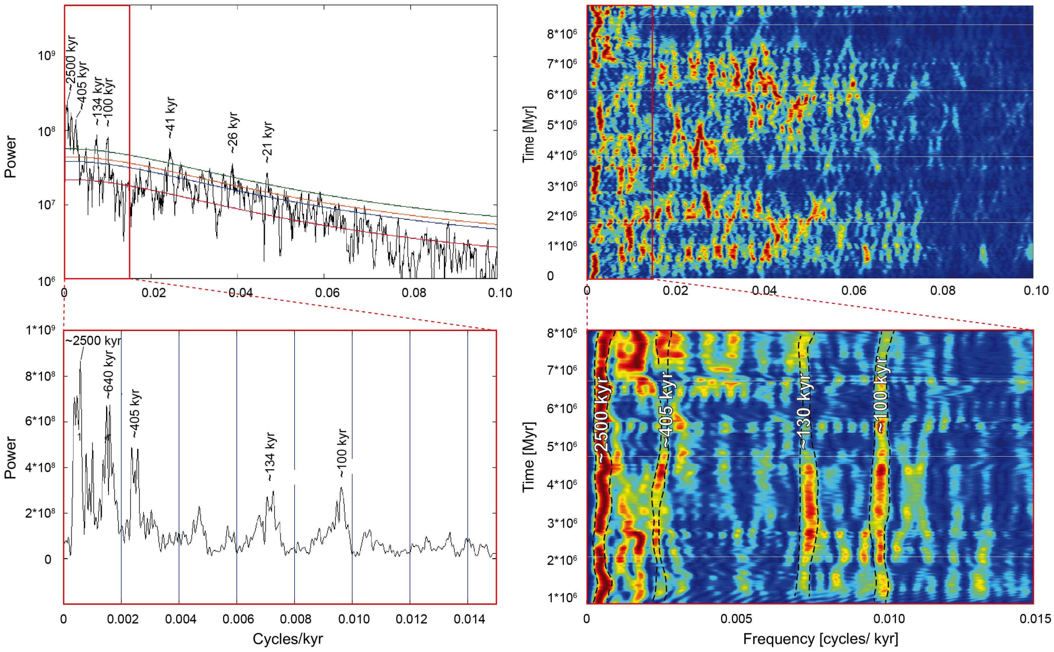

~2500 kyr
~405 kyr
~134 kyr
~100 kyr
~41 kyr
~26 kyr
~21 kyr
Power
10^9
10^8
10^7
10^6
0
0.02
0.04
0.06
0.08
0.10
Time [Myr]
8*10⁶
7*10⁶
6*10⁶
5*10⁶
4*10⁶
3*10⁶
2*10⁶
1*10⁶
0
~2500 kyr
~640 kyr
~405 kyr
~134 kyr
~100 kyr
1*10⁹
8*10⁸
6*10⁸
4*10⁸
2*10⁸
0
0.002
0.004
0.006
0.008
0.010
0.012
0.014
Cycles/kyr
~2500 kyr
~405 kyr
~130 kyr
~100 kyr
0.005
0.010
0.015
Frequency [cycles/ kyr]

FIGURE 6

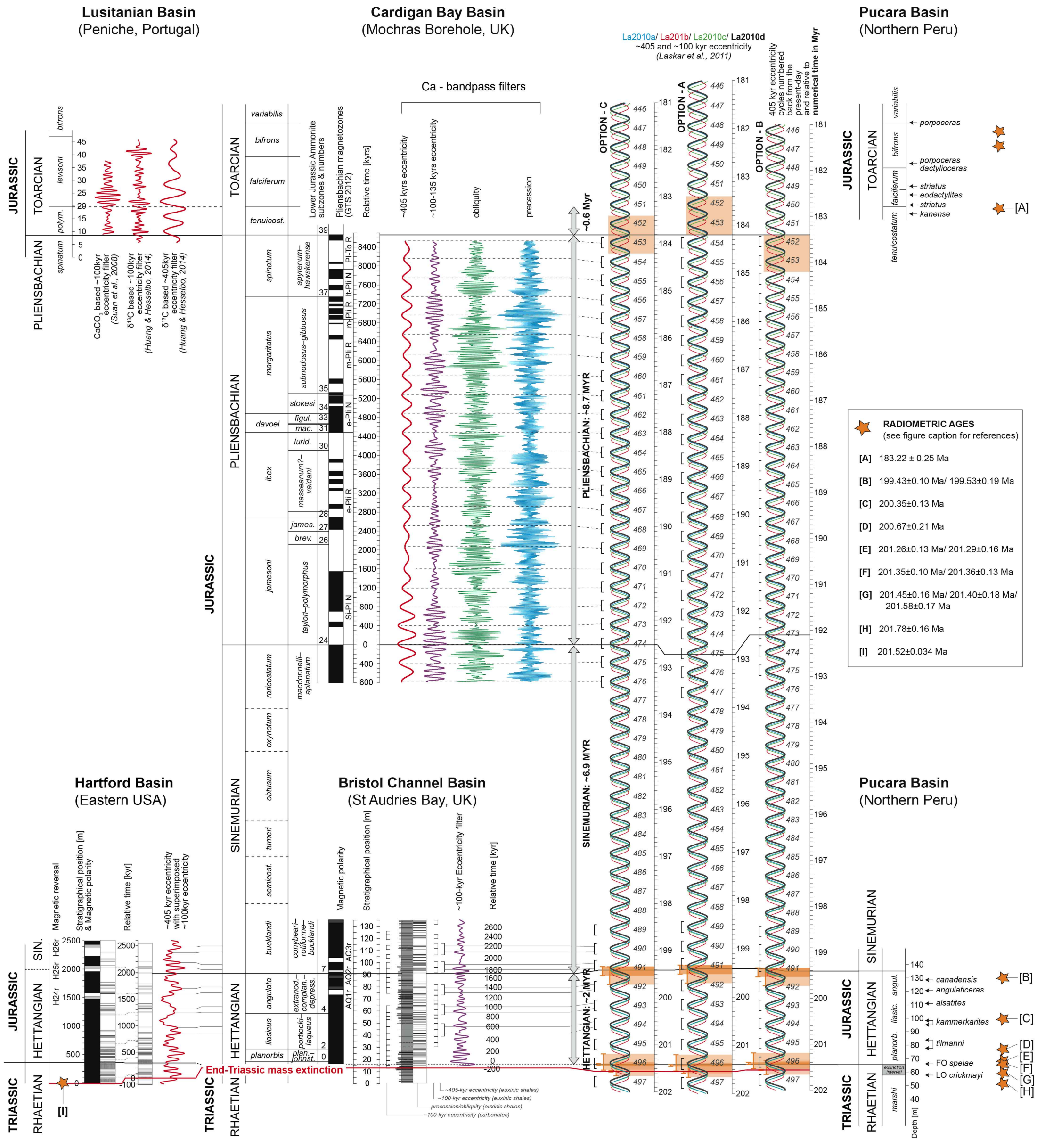

Lusitanian Basin
(Peniche, Portugal)
Cardigan Bay Basin
(Mochras Borehole, UK)
La2010a/ La201b/ La2010c/ La2010d
~405 and ~100 kyr eccentricity
(Laskar et al., 2011)
Pucara Basin
(Northern Peru)
JURASSIC
TOARCIAN
PLIENSBACHIAN
bifrons
levisoni
polym.
spinatum
CaCO3 based ~100kyr eccentricity filter (Suan et al., 2008)
δ13C based ~100kyr eccentricity filter (Huang & Hesselbo, 2014)
δ13C based ~405kyr eccentricity filter (Huang & Hesselbo, 2014)
Ca - bandpass filters
Lower Jurassic Ammonite subzones & numbers
Pliensbachian magnetozones (GTS 2012)
Relative time [kyrs]
~405 kyrs eccentricity
~100-135 kyrs eccentricity
obliquity
precession
variabilis
falciferum
tenuicost.
margaritatus
davoei
ibex
jamesoni
raricostatum
oxynotum
obtusum
turneri
semicost.
bucklandi
angulata
liasicus
planorbis
apyrenum–hawskerense
subnodosus–gibbosus
stokesi
figul.
mac.
lurid.
masseanum?–valdani
james.
brev.
taylori–polymorphus
macdonnelli–aplanatum
OPTION - C
OPTION - A
OPTION - B
405 kyr eccentricity cycles numbered back from the present-day and relative to numerical time in Myr
~0.6 Myr
PLIENSBACHIAN: ~8.7 MYR
SINEMURIAN: ~6.9 MYR
HETTANGIAN: ~2 MYR
porpoceras
porpoceras dactylioceras
striatus
eodactylites
striatus
kanense
[A]
RADIOMETRIC AGES
(see figure caption for references)
[A] 183.22 ± 0.25 Ma
[B] 199.43±0.10 Ma/ 199.53±0.19 Ma
[C] 200.35±0.13 Ma
[D] 200.67±0.21 Ma
[E] 201.26±0.13 Ma/ 201.29±0.16 Ma
[F] 201.35±0.10 Ma/ 201.36±0.13 Ma
[G] 201.45±0.16 Ma/ 201.40±0.18 Ma/ 201.58±0.17 Ma
[H] 201.78±0.16 Ma
[I] 201.52±0.034 Ma
Hartford Basin
(Eastern USA)
Bristol Channel Basin
(St Audries Bay, UK)
Magnetic reversal
Stratigraphical position [m] & Magnetic polarity
Relative time [kyr]
~405 kyr eccentricity with superimposed ~100kyr eccentricity
SIN.
HETTANGIAN
TRIASSIC
RHAETIAN
[I]
End-Triassic mass extinction
Magnetic polarity
Stratigraphical position [m]
~100-kyr Eccentricity filter
Relative time [kyr]
conybeari–rotiforme–bucklandi
extranod.–complan.–depress.
portlocki–laqueus
plan.–johnst.
~405-kyr eccentricity (euxinic shales)
~100-kyr eccentricity (euxinic shales)
precession/obliquity (euxinic shales)
~100-kyr eccentricity (carbonates)
SINEMURIAN
canadensis
angulaticeras
alsatites
kammerkarites
tilmanni
FO spelae
LO crickmayi
[B]
[C]
[D]
[E]
[F]
[G]
[H]
angul.
liasic.
planorb.
marshi
extinction interval
Depth [m]

FIGURE 7

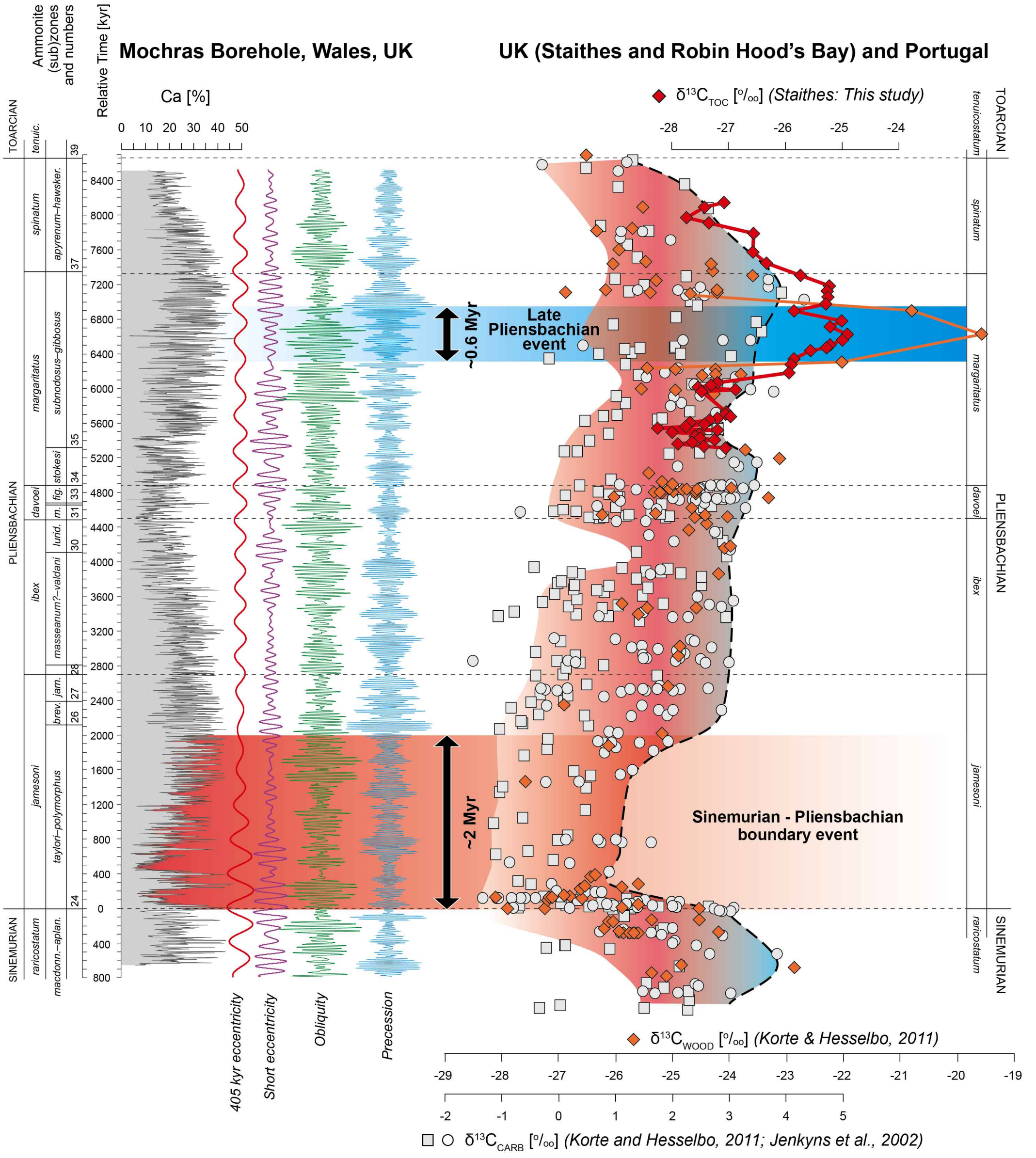

Mochras Borehole, Wales, UK
UK (Staithes and Robin Hood's Bay) and Portugal
Ammonite (sub)zones and numbers
Relative Time [kyr]
Ca [%]
0 10 20 30 40 50
δ13CTOC [‰] (Staithes: This study)
-28 -27 -26 -25 -24
TOARCIAN
PLIENSBACHIAN
SINEMURIAN
tenuic.
spinatum
margaritatus
davoei
ibex
jamesoni
raricostatum
apyrenum–hawsker.
subnodosus–gibbosus
stokesi
fig.
m.
lurid.
masseanum?–valdani
jam.
brev.
taylori–polymorphus
macdonn.–aplan.
39 37 35 34 33 31 30 28 27 26 24
8400 8000 7600 7200 6800 6400 6000 5600 5200 4800 4400 4000 3600 3200 2800 2400 2000 1600 1200 800 400 0 400 800
~0.6 Myr
Late Pliensbachian event
~2 Myr
Sinemurian - Pliensbachian boundary event
405 kyr eccentricity
Short eccentricity
Obliquity
Precession
tenuicostatum
spinatum
margaritatus
davoei
ibex
jamesoni
raricostatum
δ13CWOOD [‰] (Korte & Hesselbo, 2011)
-29 -28 -27 -26 -25 -24 -23 -22 -21 -20 -19
-2 -1 0 1 2 3 4 5
δ13CCARB [‰] (Korte and Hesselbo, 2011; Jenkyns et al., 2002)

FIGURE 8

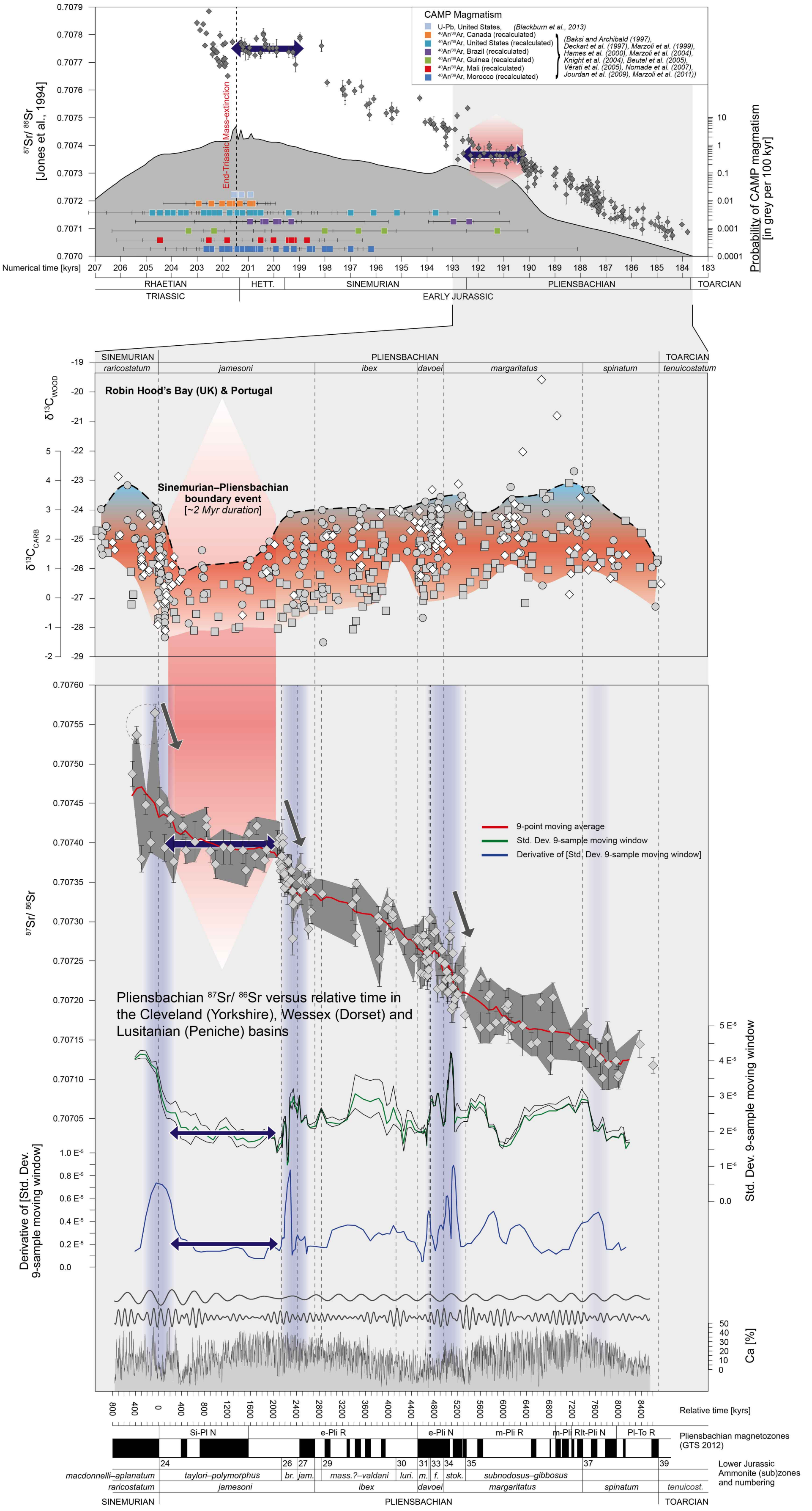

CAMP Magmatism
U-Pb, United States, (Blackburn et al., 2013)
40Ar/39Ar, Canada (recalculated)
40Ar/39Ar, United States (recalculated)
40Ar/39Ar, Brazil (recalculated)
40Ar/39Ar, Guinea (recalculated)
40Ar/39Ar, Mali (recalculated)
40Ar/39Ar, Morocco (recalculated)
(Baksi and Archibald (1997), Deckart et al. (1997), Marzoli et al. (1999), Hames et al. (2000), Marzoli et al. (2004), Knight et al. (2004), Beutel et al. (2005), Vérati et al. (2005), Nomade et al. (2007), Jourdan et al. (2009), Marzoli et al. (2011))
87Sr/86Sr [Jones et al., 1994]
0.7079
0.7078
0.7077
0.7076
0.7075
0.7074
0.7073
0.7072
0.7071
0.7070
End-Triassic Mass-extinction
Probability of CAMP magmatism [in grey per 100 kyr]
10
1
0.1
0.01
0.001
0.0001
Numerical time [kyrs]
207 206 205 204 203 202 201 200 199 198 197 196 195 194 193 192 191 190 189 188 187 186 185 184 183
RHAETIAN
HETT.
SINEMURIAN
PLIENSBACHIAN
TOARCIAN
TRIASSIC
EARLY JURASSIC
SINEMURIAN
PLIENSBACHIAN
TOARCIAN
raricostatum
jamesoni
ibex
davoei
margaritatus
spinatum
tenuicostatum
δ13CWOOD
-19 -20 -21 -22 -23 -24 -25 -26 -27 -28 -29
δ13CCARB
5 4 3 2 1 0 -1 -2
Robin Hood's Bay (UK) & Portugal
Sinemurian–Pliensbachian boundary event
[~2 Myr duration]
87Sr/86Sr
0.70760
0.70755
0.70750
0.70745
0.70740
0.70735
0.70730
0.70725
0.70720
0.70715
0.70710
0.70705
9-point moving average
Std. Dev. 9-sample moving window
Derivative of [Std. Dev. 9-sample moving window]
Pliensbachian 87Sr/86Sr versus relative time in the Cleveland (Yorkshire), Wessex (Dorset) and Lusitanian (Peniche) basins
Std. Dev. 9-sample moving window
5 E-5
4 E-5
3 E-5
2 E-5
1 E-5
0.0
Derivative of [Std. Dev. 9-sample moving window]
1.0 E-5
0.8 E-5
0.6 E-5
0.4 E-5
0.2 E-5
0.0
Ca [%]
50 40 30 20 10 0
800 400 0 400 800 1200 1600 2000 2400 2800 3200 3600 4000 4400 4800 5200 5600 6000 6400 6800 7200 7600 8000 8400
Relative time [kyrs]
Si-Pl N
e-Pli R
e-Pli N
m-Pli R
m-Pli
Rlt-Pli N
Pl-To R
Pliensbachian magnetozones (GTS 2012)
24 26 27 29 30 31 33 34 35 37 39
macdonnelli–aplanatum
taylori–polymorphus
br.
jam.
mass.?–valdani
luri.
m.
f.
stok.
subnodosus–gibbosus
raricostatum
jamesoni
ibex
davoei
margaritatus
spinatum
tenuicost.
Lower Jurassic Ammonite (sub)zones and numbering
SINEMURIAN
PLIENSBACHIAN
TOARCIAN

TABLE 1

Table 1: Early Jurassic Stage and ammonite zone ages and durations

Stage	Ammonite Zone	Base Age [Myr]	Base age: radiometric and astrochronological uncertainty [Myr]	Mochras Borehole: base biostratigraphic uncertainty [Myr]	Duration and biostratigraphic uncertainty [Myr]
	tenuicostatum	183.8	+/-0.4	+0.25	~0.6
Toarcian		**183.8**	**+/-0.4** *(combined astrochr./ radiom. uncertainty)*	**+0.25**	**~8.3**
	spinatum	185.2	+/-0.4 *(extrapolated from above)*	+0.25	~1.4 (+0.25/-0.25)
	margaritatus	187.6	+/-0.4 *(extrapolated from above)*	0	~2.4 (-0.25)
	davoei	188.0	+/-0.4 *(extrapolated from above)*	0	~0.4
	ibex	189.8	+/-0.4 *(extrapolated from above)*	0	~1.8
	jamesoni	192.5	+/-0.4 *(extrapolated from above)*	+0.15	~2.7 (+0.15)
Pliensbachian		**192.5**	**+/-0.4** *(extrapolated from above)*	**+0.15**	**~8.7 (+0.15/-0.25)**
	raricostatum				> 0.8
	oxynotum				
	obtusum				
	turneri				
	semicostatum				
	bucklandi	199.43	+/-0.1 *(radiometric uncertainty)*		> 1.1
Sinemurian		**199.43**	**+/-0.1** *(radiometric uncertainty)*		**6.93 (+0.75/-0.65)**
	angulata	~200.25			~0.82
	liasicus	~201.04			~0.79
	planorbis	~201.35			~0.31
Hettangian	*spelae*	**201.42**	**+/-0.02** *(radiometric uncertainty)*		**1.99 (+/-0.12)**

Supplementary Materials

ASTRONOMICAL CONSTRAINTS ON THE DURATION OF THE EARLY JURASSIC PLIENSBACHIAN STAGE AND GLOBAL CLIMATIC FLUCTUATIONS

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[1] ANALYTICAL METHODS

High-resolution (10–15 cm) elemental concentrations (e.g. Ca, Ti, Fe, Rb, Zr) were obtained by hand-held X-ray fluorescence (XRF) analyses on the slabbed archive half of the Mochras core, from the late Sinemurian *raricostatum* zone (starting at 1284.08 m in the *macdonnelli–aplanatum* subzone) to the Early Toarcian *tenuicostatum* zone (up to a depth of 861.32 m). XRF analyses were conducted with a Thermo Scientific Niton XLT instrument, with a 50-sec measurement window, in soil mode. Long-term drift in measurement values was counteracted by regular internal calibration. Internal measurement uncertainty, partly due to internal calibration and Compton normalization, differs between elements and is reported in Table 1. Long-term drift in analyses was further checked by repeated analysis of the NIST2780 and NIST2709 international reference standards. Repeated analysis of the NIST2780 standard showed for calcium (Ca) an average of 1426 ppm, with a standard deviation (StDev) of 205 ppm and an average internal error of 112 ppm, and for iron (Fe) an average of 28395 ppm, with a standard deviation of 240 ppm and an average internal error of 216 ppm. Repeated analysis of the NIST2709 standard showed for calcium an average of 21130 ppm, with a standard deviation of 362 ppm and an average internal error of 476 ppm, and for Fe an average of 34678 ppm, with a standard deviation of 382 ppm and an average internal error of 454 ppm. Reproducibility of XRF-based calcium concentration data was further confirmed by comparison to Rock-Eval derived calcium carbonate content ($CaCO_3$; calculated from mineral carbon) (Supplementary Figure 1).

Rock-Eval analysis was performed with the Rock-Eval VI unit from Vinci Technologies, at the department of Earth Sciences, University of Oxford. Samples were homogenised and ~50 mg of sample was subsequently analysed by heating (with incremental temperature increases from room temperature to up to 850°C) in the oxidation and pyrolysis ovens. Mineral carbon content was calculated from the $S3_{MINC}$ and S5 peaks, resulting from the CO and CO_2 flux from the sample and analysed by infrared detector. The TOC content was simultaneously obtained in the same sample-run and was calculated from the combined CO and CO_2 fluxes representing the Pyrolysable Carbon (PC: $S1 + S2 + S3_{CO} + S3_{CO2}$) and the Residual Carbon (RC: $S4_{CO} + S4_{CO2}$). Precision and accuracy of the Rock-Eval analyses was checked by regular measurement of the in-house standard SAB134 (a Lower Jurassic shale) and the international reference standard IFP160000. Repeated long-term analyses of the mineral carbon content of the in-house SAB134 standard shows an average of 5.97%, with a StDev of 0.37%. These values include all outliers; performance is generally better, with an average concentration of 6.03% and a StDev of 0.11%. Repeated long-term analyses of the mineral carbon content of the IFP160000 standard shows an average concentration of 3.20%, with a StDev of

0.02% (the mineral carbon concentration of this standard is referenced at 3.26 ± 0.12%). Repeated long-term analyses of the TOC content of the in-house SAB134 standard shows an average of 2.87%, with a StDev of 0.39%. These values include all outliers; performance is generally better, with an average concentration of 2.80% and a StDev of 0.11%. Repeated long-term analyses of the TOC content of the IFP160000 standard showed an average concentration of 3.27%, with a StDev of 0.04% (the TOC content of this standard is referenced at 3.28 ± 0.14%).

Calcium concentration spot-analysis by XRF was performed on the slabbed core, whereas $CaCO_3$ analysis (calculated from the mineral carbon content) by Rock Eval was performed on homogenised 1 cm^3 samples from stratigraphically nearby (within a few cm), but different, depth intervals (Supplementary Figure 1). Despite this minor stratigraphic offset, calculated calcium concentrations from Rock Eval and adjacent XRF measurements still correlate well (with $R^2 > 0.75$) (Supplementary Figure 1). Additionally, minor offsets between the Ca-concentration from XRF analyses and the calculated Ca-concentration, based on the mineral carbon content measured by Rock-Eval, may also derive from the presumption that carbonate minerals are all associated with calcite, as $CaCO_3$. Some of the carbonate minerals in the host-rock may exist as dolomite or siderite, rather then calcium carbonate. The combined internal error on XRF-based Ca analysis and Rock Eval-based $CaCO_3$ analysis was at any time 1–2 orders of magnitude smaller than the observed variability between the mudstone/marl and the calcareous mudstone/limestone in the Mochras core.

Analysis of $\delta^{13}C_{TOC}$ was performed on decarbonated and homogenized Upper Pliensbachian outcrop samples from Staithes (Yorkshire; locality described in Korte and Hesselbo (2011)). One gram of homogenized sample material was decarbonated twice with 3 M HCl in a warm water bath at 80 °C for 5 hours. The sample was subsequently rinsed three times with Milli-Q water to reach neutral *p*H levels. Between 1–10 mg of decarbonated sample (aiming for ~25 μg pure carbon) was then weighed into 8×5 mm thin capsules for $\delta^{13}C_{TOC}$ analyses. $\delta^{13}C_{TOC}$ analyses were performed at the School of Archaeology (University of Oxford) and at the Stable Isotope Laboratory at the Open University (Milton Keynes, UK), with a Thermo Scientific Flash 2000 HT Elemental Analyser (EA) coupled to a Thermo Scientific MAT253 isotope ratio mass spectrometer via a Conflo IV open split interface. The Thermo Scientific Flash 2000 HT EA has a MAS2000 carousel and, between the carousel and the EA, sits a Thermo No Blank Device (NBD), allowing for the single sample purging with helium. The EA is also equipped with a Thermal Conductivity Detector (TCD). Automated dilution of sample gas with the Conflo IV open split interface allowed for high dynamic range of C (+N) content and controlled the introduction of the reference gases. Analytical precision at the Open University was checked by routine analysis of three internal and referenced laboratory standards, urea 020914MAG, glutamic acid light and Alanine-A, which give measured average $\delta^{13}C$ values of –43.9‰, –25.1‰ and –22.2‰, respectively, with standard deviations of 0.3‰, 0.2‰ and 0.1‰. Analytical precision for $\delta^{13}C_{TOC}$ analyses at the Universty of Oxford was checked by routine analysis of the Alanine-B international reference standard, which showed average $\delta^{13}C_{TOC}$ of –26.9‰, with a StDev of 0.1‰ (the Alanine-B standard is referenced at -26.65‰). Isotope ratios are reported in standard delta notation relative to Vienna PDB.

[2] SUPPLEMENTARY FIGURE CAPTIONS

SUPPLEMENTARY FIGURE 1 Comparison of hand-held X-ray fluorescence (blue) and Rock Eval-based (red) calcium (Ca) concentrations in a selected part of the Mochras Core. Note that analyses are not performed on the same stratigraphic sample-depths. Black dots give the stratigraphic difference in centimetre between a Rock-Eval measurement and the stratigraphically nearest hand-held XRF analyses. Despite the Rock-Eval and hand-held XRF analyses on stratigraphically different (but nearby) samples, the obtained Ca concentrations correlate well, with an R^2 of ~0.75.

SUPPLEMENTARY FIGURE 2 XRF-derived Ca-concentrations across the Sinemurian-Pliensbachian boundary are plotted on top of the stacked core-photos showing clear correlation between elevated Ca-concentrations and lighter-grey sedimentary horizons. Mineral carbon content, derived by Rock-Eval analyses, closely matches fluctuations in Ca-concentrations. TOC and HI values, derived from Rock-Eval analyses negatively correlate to Ca and mineral-carbon concentrations.

SUPPLEMENTARY FIGURE 3 Scanning Electron Microscopy (SEM) backscatter pictures of (A) a calcareous mudstone (depth: 842.04 m core-depth below surface) with fine silt-sized detrital calcite grains circled in red dashed line and (B) a limestone interval (depth: 807.19 m core-depth below surface), with a massive calcium carbonate matrix and some replacement by quartz.

SUPPLEMENTARY FIGURE 4 Multi-taper (MTM) spectral analyses of the obtained XRF elemental (Ca) depth series using the Astrochron (R (3.1.2) Package for astrochronology, version 0.3.1) toolkit (Meyers, 2014). (A) Multi-taper (MTM) power spectrum of the complete Pliensbachian (uppermost *raricostatum* to lowermost *tenuicostatum*) Ca record, showing clear dominance of the >150m periodicity. (B) Multi-taper (MTM) power spectrum of the complete detrended (high band-pass filter (<150m)) Pliensbachian (uppermost *raricostatum* to lowermost *tenuicostatum*) Ca-record. (C) Multi-taper (MTM) power spectrum of the detrended (high band-pass filter (<150m)) uppermost *raricostatum* to lower *margaritatus* Ca-record. (D) Multi-taper (MTM) power spectrum of the detrended (high band-pass filter (<150m)) upper *margaritatus* to lowermost *tenuicostatum* Ca record. Note the order of magnitude differences in Linear Power for the MTM Power estimates, especially for Figure D.

SUPPLEMENTARY FIGURE 5 Multi-taper (MTM; 3π) spectral analyses of the obtained XRF elemental (Fe and Ca) time series using the Astrochron (R (3.1.2) Package for astrochronology, version 0.3.1) toolkit (Meyers, 2014), with robust red noise models (Mann and Lees, 1996). The elemental Fe record was first manipulated to give uniform sample spacing using linear interpolation. Initial spectral analysis was performed with AnalySeries on a detrended data-series (with low band-pass filtering to remove >150 m periodicities). Dominant spectral components (Supplementary Figure 3) were subsequently filtered from the data series and compared to the visually defined precession and short- and long-eccentricity periodicities (Figure 3). The elemental Ca record in the depth domain was subsequently converted to the time domain following the observed 405 kyr eccentricity cycles. The multi-taper (MTM; 3π) spectral analyses of the obtained elemental (Fe and Ca) time-series show dominant and significant peaks at precession, obliquity, and short- and long-period eccentricity. MTM power estimates, AR1 confidence level estimates and harmonic test confidence level estimates are performed with the Astrochron (R (3.1.2) Package for astrochronology, version 0.3.1) toolkit (Meyers, 2014). An independent check of the dominant spectral components is performed with AnalySeries 2.0.8 (Paillard et al., 1996), giving a 80% confidence interval (grey).

SUPPLEMENTARY FIGURE 6 Precession (blue), obliquity (green), 100–135 kyr eccentricity (purple) and 405 kyr eccentricity (red) band-pass filters, reflecting frequency intervals in the MTM power spectra (Supplementary Figure 4) of the detrended (high band-pass) Fe and Ca time series.

SUPPLEMENTARY FIGURE 7 Comparison of the Pliensbachian stratigraphic depth record with the obtained Pliensbachian time series shows a pronounced 40–60% decrease in sedimentation rate in the upper *margaritatus* ammonite zone (starting at ~918m core depth). Lower Jurassic (top Sinemurian to base Toarcian) ammonite genera occurrence is based on Woodland (1971). Blue bars represent the occurrence of ammonite genera, with a specific genus occurring within a 20 feet (6.096m) window (Woodland, 1971). Minor refinements on ammonite zone boundary positions are based on Copestake and Johnson (2014), which are followed here. Many ammonite (sub)zone boundaries are constrained by first and last occurrences of ammonite genera. Some (sub)zone boundaries are potentially less well constrained, as recognized by a grey bar.

SUPPLEMENTARY FIGURE 8 Lower Pliensbachian (*jamesoni* ammonite zone) $^{87}Sr/^{86}Sr$ data plotted in time in kyrs, (A) based on the Mochras-core derived Pliensbachian time-scale as presented in Figure 8 of the main-text, (B) based on the Belemnite Marls (Dorste, UK) derived Lower Pliensbachian time-scale as presented in Weedon and Jenkyns (1999), and (C) assuming equal duration of Pliensbachian ammonite zones. The Early Pliensbachian $^{87}Sr/^{86}Sr$ record in the time-domain shows a plateau, with relatively constant values, throughout the *taylori-polymorphus* ammonite subzones, followed by a rapid drop in the *brevispina* ammonite subzone, based on both the Mochras and the Belemnite Marl derived time-scales. (D) MTM Power spectrum of the tuned *jamesoni*-ammonite zone % Ca-record of the Mochras core, based on the Mochras-time-scale (this study), and (E) the tuned *jamesoni*-ammonite zone % Ca-record of the Mochras core, based on the Belemnite Marl time-scale of Weedon and Jenkyns (1999), following similar methods and parameters as presented in Supplementary Figures 4 and 5. (D) Clear peaks on expected astronomical frequencies, while peaks in (E) show no resemblance to astronomical frequencies as known from the geological record and astronomical solutions. This inconsistency suggests that the Lower Pliensbachian time-scale based on the Belemnite Marls is incorrect, which can be largely explained by the observed sedimentary hiatuses at the base of the *jamesoni* ammonite subzone and possibly within the *brevispina* ammonite subzone.

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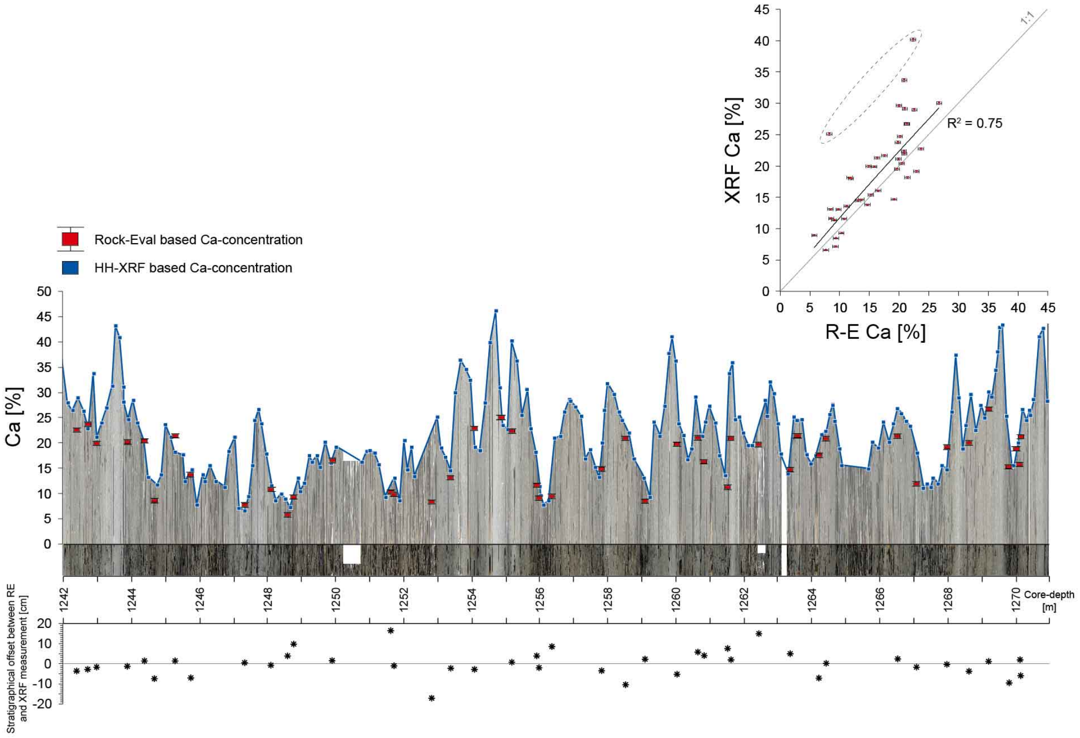
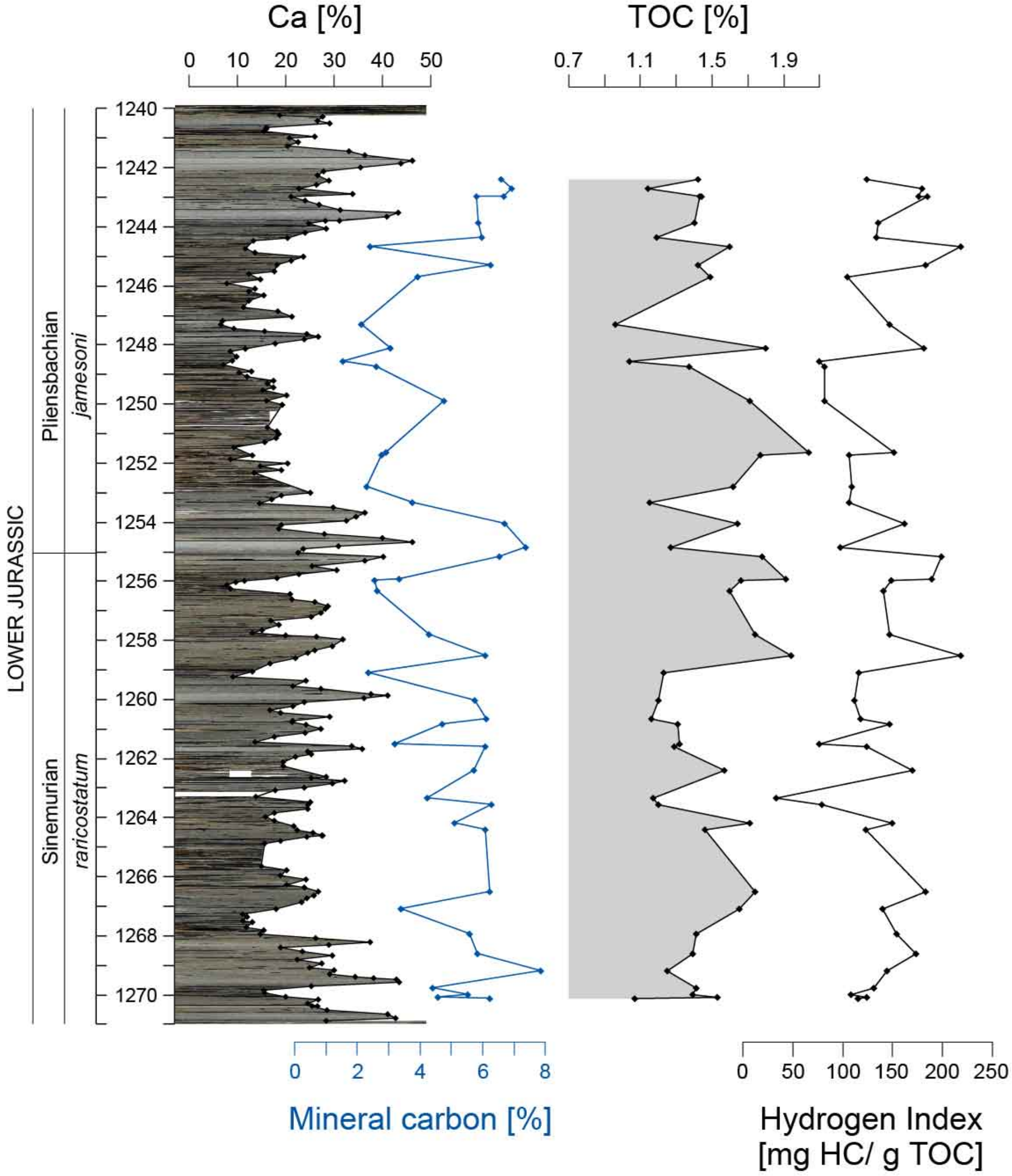
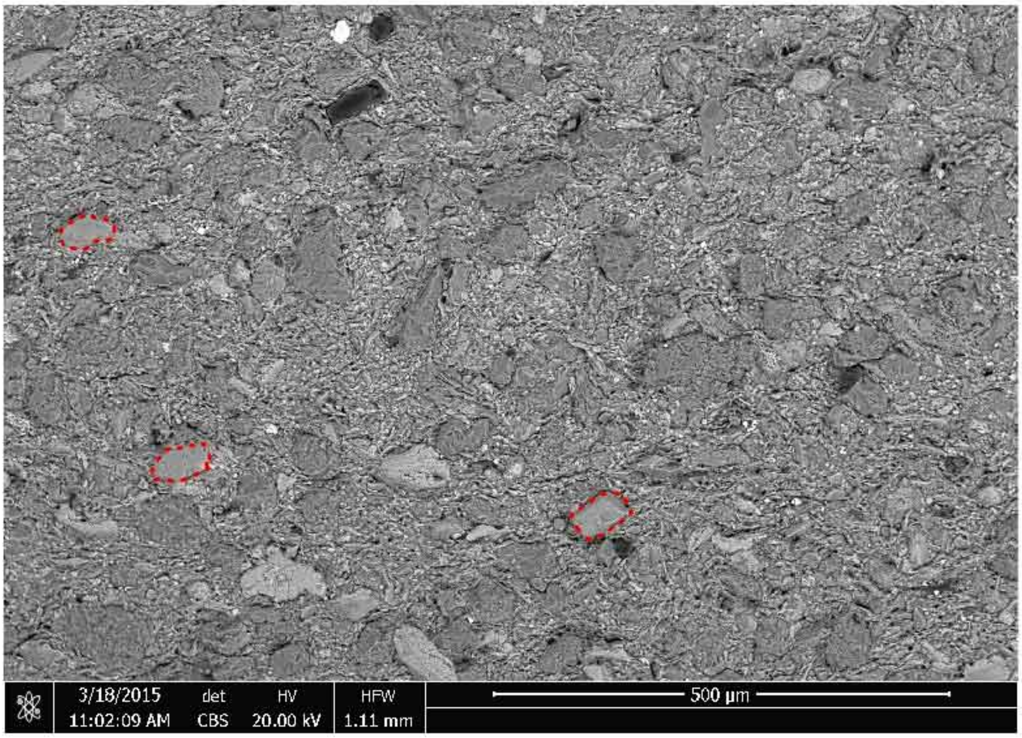
SUPPLEMENTARY FIGURE 1



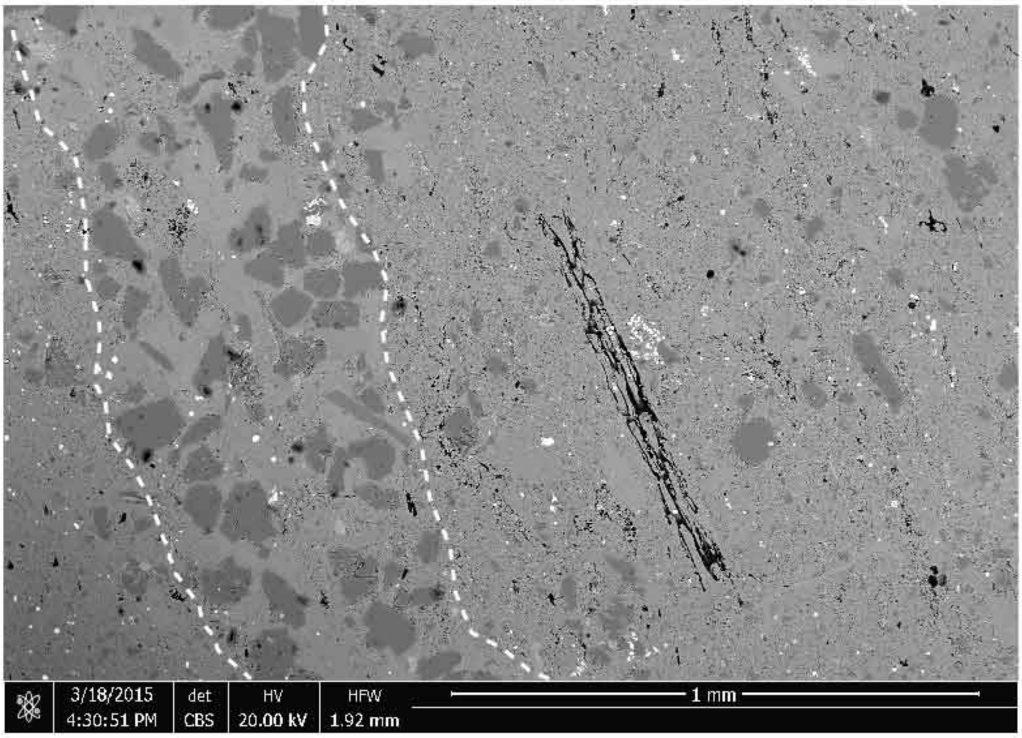
SUPPLEMENTARY FIGURE 2



SUPPLEMENTARY FIGURE 3

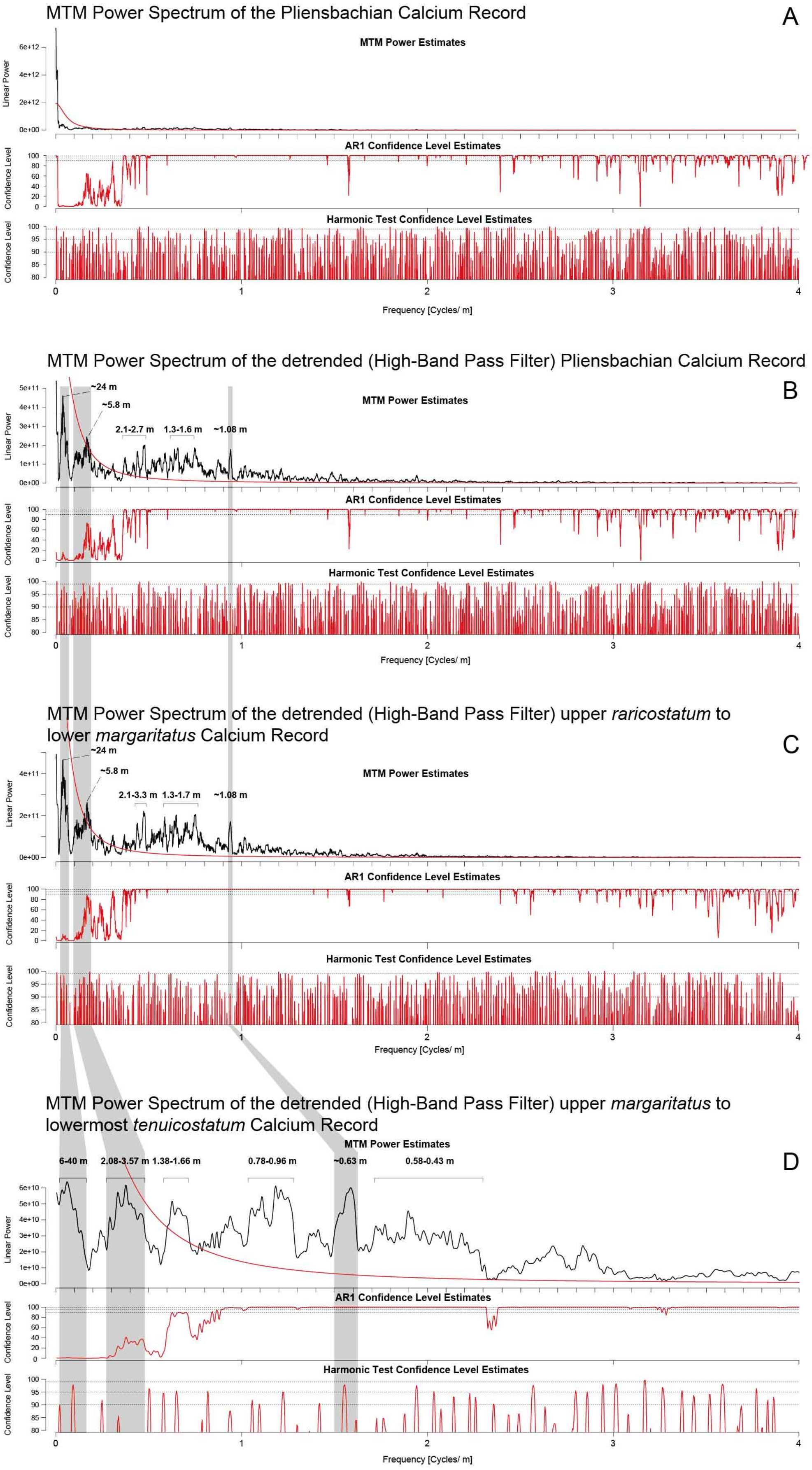


A: Fine silty sized detrital calcite grains circled in red dashed line



B: Fossil-shell fragment (marked by the white dashed line), which is partly replaced by quartz. The shell fragment and a woody clast (in black) are embedded in a likely early diagenetic massive calcium carbonate matrix.

SUPPLEMENTARY FIGURE 4



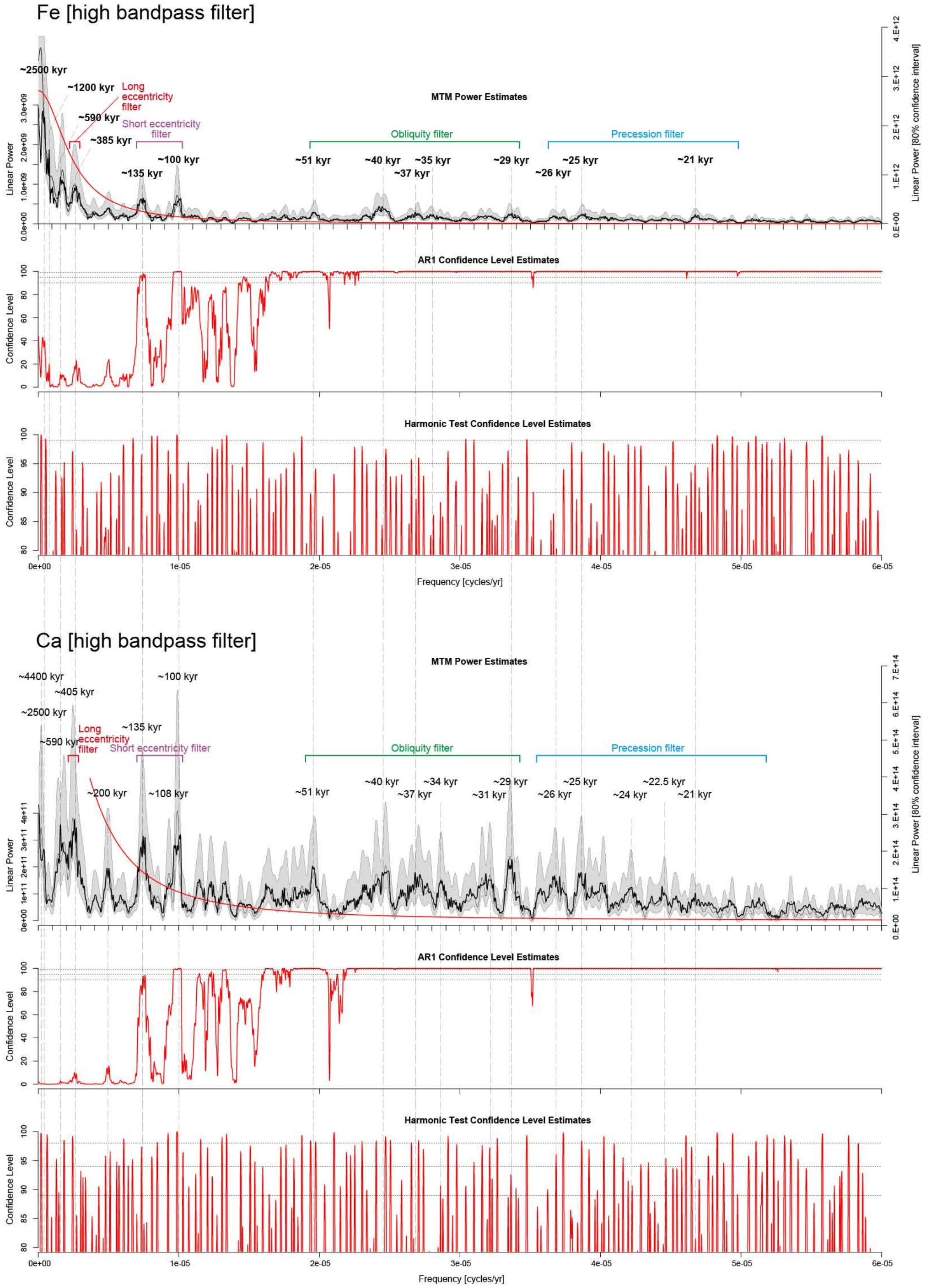
MTM Power Spectrum of the Pliensbachian Calcium Record

MTM Power Spectrum of the detrended (High-Band Pass Filter) Pliensbachian Calcium Record

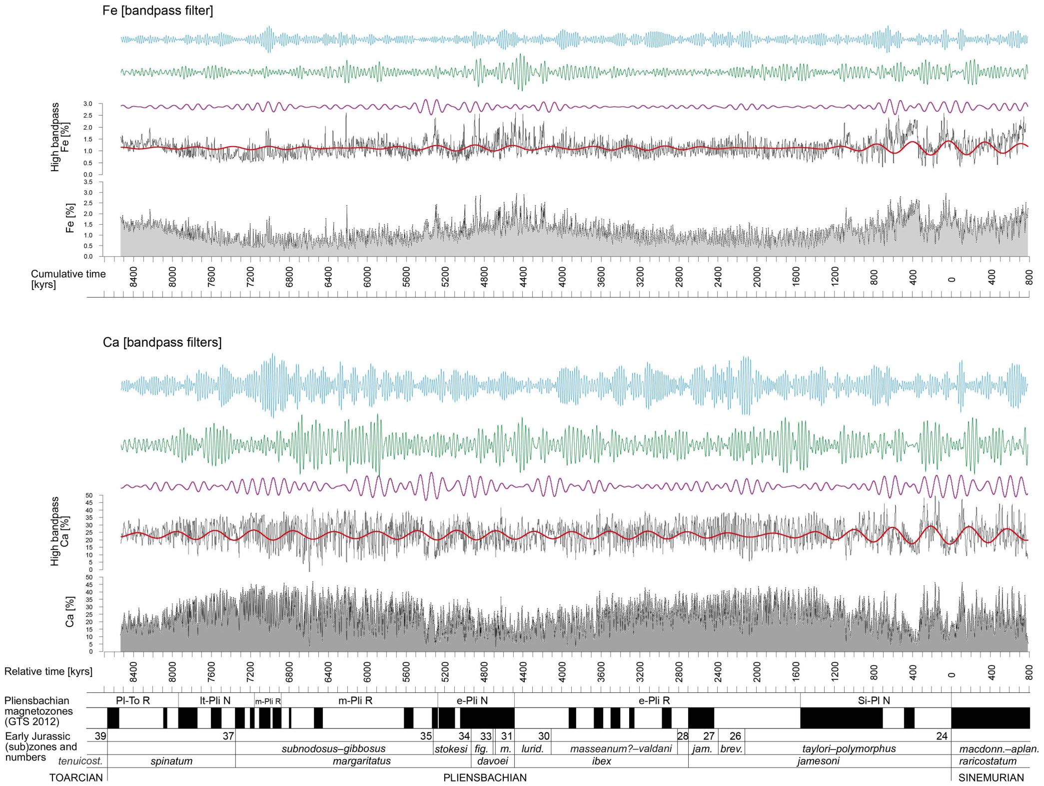
MTM Power Spectrum of the detrended (High-Band Pass Filter) upper *raricostatum* to lower *margaritatus* Calcium Record

MTM Power Spectrum of the detrended (High-Band Pass Filter) upper *margaritatus* to lowermost *tenuicostatum* Calcium Record

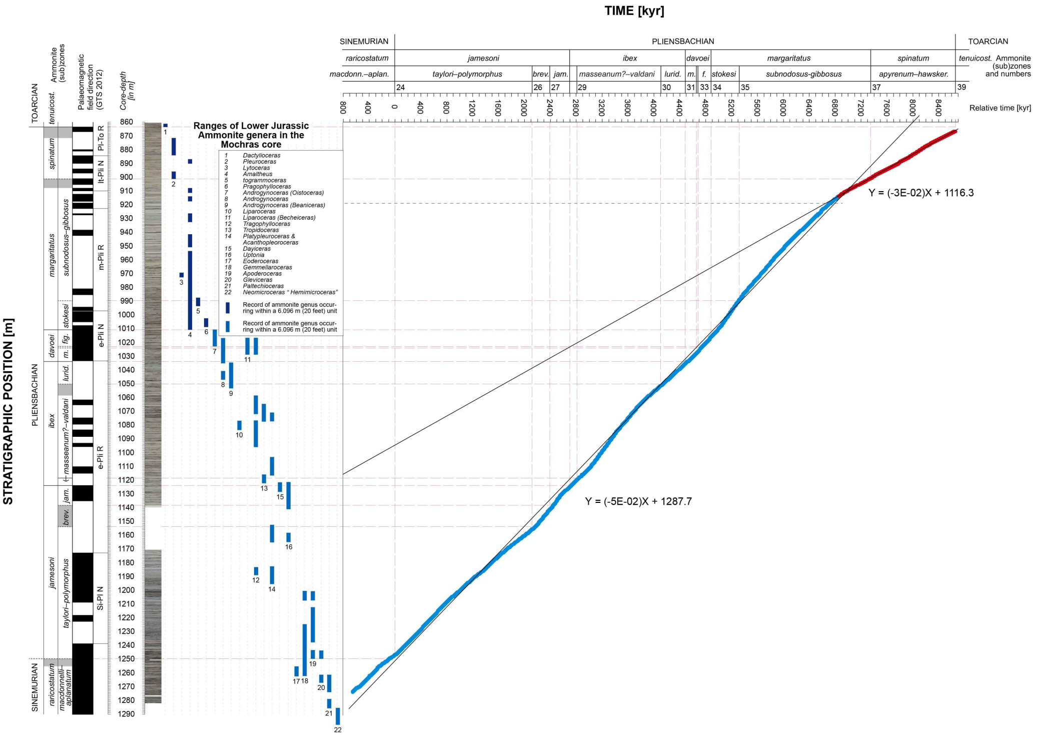
SUPPLEMENTARY FIGURE 5



SUPPLEMENTARY FIGURE 6



SUPPLEMENTARY FIGURE 7



SUPPLEMENTARY FIGURE 8