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

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Keywords: astrochronology, carbon-cycle, cyclostratigraphy, Early Jurassic, Pliensbachian, strontium isotopes

ABSTRACT

The Early Jurassic was marked by multiple periods of major global climatic and palaeceanographic 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 δ13C 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 87Sr/86Sr record shows relatively stable values during the first ~2 Myr of the Pliensbachian, superimposed on the long-term Early Jurassic decline in 87Sr/86Sr. This plateau in 87Sr/86Sr 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 87Sr/86Sr.

[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 (δ13C) 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 δ13C of wood (δ13Cwood), and up to 3‰ in the δ13C of organic matter
(δ13CTOC; TOC: Total Organic Carbon) (Figure 7; Suan et al., 2010; Korte & Hesselbo,
2011; Silva et al., 2011), reflecting enrichment of 13C 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 δ18Ocalcite,
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 *rariostratum* zone to the Lower Toarcian *teniostatium*
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 Staithe, (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 PLIENSCHABIAN 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 CaCO₃) and is especially prominent around the Sinemurian–Pliensbachian boundary (rariostatum 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 diageneric element enrichment may also have affected the carbonate-silicate balance. It is reasonable to conclude that diagensis 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 diageneric 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 (E₁) 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 (E₁), each consisting of 4–5 lithological couplets, occur in one super-bundle (E₂). The observed couplets, bundles (E₁) and super-bundles (E₂) 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 (E₁) and super-bundles (E₂) (Figures 3, 4). This procedure allows for independent comparison to Milankovitch periodicities assigned from subsequent spectral and multi-taper analyses. Some of the E₁-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 E₂-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 3t 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 high frequency 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') and
super-bundles (E''), 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 *tennicostatum* 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') and super-bundles (E'')
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
PLIENSCHACHIAN 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 lowest 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 δ13C (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).
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 $^{87}\text{Sr}/^{86}\text{Sr}$ (McArthur et al., 2000). This does, however, not infer that a linear change in $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{238}\text{U}/^{206}\text{Pb}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ (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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$-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 *earlattense* 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 *tenuncostatum* 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 *crassostoa* zone (which slightly post-dates the onset of the European *variabilis* ammonite zone) (Pálfiy 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 Plänsbachian to the numerical time scale (Figure 6).

The *falciferum* ammonite zone follows the lowest Toarcian *tenuncostatum* zone in northwest Europe and the age-equivalent *polymorphum* zone in the Lusitanian Basin of Portugal. The duration of the *polymorphum* (and *tenuncostatum*) 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 90–50 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 *tenuncostatum*–*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* (*tenuncostatum*) 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 *tenuncostatum* 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 (δ13C) and other geochemical proxy records. Seawater 87Sr/86Sr-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 stage (~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 *tenuirostratum* 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 0 argument \((θ = (s_i - s_j) - 2(g_i - g_j))\), where \(g_i\) and \(s_i\) are related to precession of the perihelion and \(s_i\) and \(g_i\) are related to precession of the node of Earth and Mars (Laskar et al., 2004, 2011). The 405 Kyr eccentricity cycle, related to the \((g_i - g_j)\) 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 PLIENSBOCHIAN 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 δ¹³C (of 2–4‰) in marine
calciite 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 δ¹³C 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 δ¹³C of marine and terrestrial
organic matter, marine calciite 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 pCO₂,
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) δ¹³C 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 ⁸⁷Sr/⁸⁶Sr
RECORD

Seawater ⁸⁷Sr/⁸⁶Sr 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 ⁸⁷Sr/⁸⁶Sr 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 *Ptiloceras spelea* (tirolicum) (and *Ptiloceras spelea* (speleu)), 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 evaporites, 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 40Ar/39Ar (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 87Sr/86Sr 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 87Sr/86Sr values (Cohen and Coe, 2007). However, this supposed constant rate of decline in seawater 87Sr/86Sr may be an artefact of the assumption of equal duration ammonite (sub-)zones. Conversion of the Pliensbachian seawater 87Sr/86Sr 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 87Sr/86Sr 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 foraminifer zones (Copestake and Johnson, 2013).

Phases of enhanced decline in seawater 87Sr/86Sr 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 87Sr/86Sr 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 87Sr/86Sr 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 87Sr/86Sr 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 87Sr/86Sr 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 87Sr/86Sr ratios depends on (1) the correct biostratigraphical correlation between the 87Sr/86Sr 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 $p$CO$_2$
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
$\delta^{13}$C/$\delta^{18}$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 $jibec$, ~0.4 Myr $dawoe$, ~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 $\delta^{13}$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 $\delta^{13}$C, which coincides
with a seawater cool phase in the European realm as revealed by $\delta^{18}$O from macrofossil
calcite, has a duration of ~0.6 Myr.

Calibration of the Pliensbachian $\delta^{13}$C/$\delta^{18}$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
$\delta^{13}$C/$\delta^{18}$Sr record also shows a stable plateau in the Early Pliensbachian $jamesoni$ zone,
coinciding with the observed $\delta^{13}$C negative shift of 2–4‰, and possibly reflecting
 elevated continental weathering, with a relatively increased flux of radiogenic $\delta^{13}$C/$\delta^{18}$Sr to
the global oceans, in response to a late phase of enhanced global continental (silicate)
weathering induced by CAMP volcanism.

ACKNOWLEDGEMENTS

We acknowledge funding for this study from Shell International Exploration &
Production B.V., the International Continental Drilling Programme, and the Natural
Environment Research Council (NE/G01700X/1). CVU acknowledges funding from
Leopoldina, German National Academy of Sciences (grant no. LPDS 2014-08). We
thank the British Geological Survey (BGS) for enabling access to the Mochras core and
Charles J.B. Gowing (BGS) for supplying hand-held XRF equipment and assistance with
analyses. We also thank Steve Wyatt (Oxford) and Mabs Gilmour (Open University) for
help with Rock-Eval and $\delta^{13}$C analyses. We are further grateful for the constructive
reviews by Wolfgang Ruebsam, Blair Schoene and one anonymous reviewer, and the
editorial guidance by Martin Frank. JBR publishes with the approval of the Executive
Director, British Geological Survey (NERC).

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 (E1) and super-bundles (E2), 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 *tenniostatum* 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 *davei* 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 of *falciferum* zone in the Pucara Basin in Peru and the ~200 Kyr uncertainty in the astrochronologically estimated duration of the base Toarcian *polymorphum* (*tenricostatum*) 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. (2012), Blackburn et al. (2013), Huang and Hesselbo (2014), Hüssing 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 Hüssing et al. (2014). The Pliensbachian palaeomagnetic record is from the Geological Time Scale (GTS) 2012 (Gradstein et al., 2012).

**FIGURE 7** The Pliensbachian δ¹³C record of marine calcite and wood from UK outcrops (Jenkyns et al., 2002; Korte and Hesselbo, 2011) and δ¹³C of bulk organic matter (δ¹³C(Tot) 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 ⁸⁷Sr/⁸⁶Sr record calibrated against the newly derived floating astrochronological time scale, using subzone boundaries in outcrops (that yielded ⁸⁷Sr/⁸⁶Sr data) and the Mochras core as tie-points, and linear interpolation within subzones. The time-calibrated ⁸⁷Sr/⁸⁶Sr 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 ⁸⁷Sr/⁸⁶Sr (blue arrows), coinciding with a global carbon-cycle perturbation and recurrent Central Atlantic Magmatic Province (CAMP) volcanism. Early Jurassic ⁸⁷Sr/⁸⁶Sr 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 δ¹³C 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 ⁴⁰Ar/³⁹Ar radiometric dates of individual basalt formations.

**TABLE 1** Absolute age, uncertainty and duration estimates for the (base of the Early Jurassic stages (Hettangian, Sinemurian, 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), Bouilla et al. (2014), Huang and Hesselbo (2014), Hüssing et al. (2014), Ruebsam et al., 2014 and Sell et al. (2014).

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Sambrotto, R.N., Compound
d

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Von Hillebrandt, A.V., Krystyn, L., Kürschner, W.M., Bonis, N.R., Ruhl, M., Richoz, S.,

Schoffen, M.A.N., Urlichs, M., Bown, P.R., Kment, K., McRoberts, C.A., Simms, M.,


FIGURE 3
FIGURE 4

Astronomically calibrated Plenusbachian ammonite zone durations:

- *jamesoni* zone: ~2.7 Myr
- *laxa* zone: ~1.8 Myr
- *alaris* zone: ~0.4 Myr
- *margaritatus* zone: ~2.4 Myr
- *sphenarium* zone: ~1.4 Myr
FIGURE 5
FIGURE 7

Mochras Borehole, Wales, UK

UK (Staithes and Robin Hood’s Bay) and Portugal

Ca [%]

δ¹³Corg [%‰] (Staithes: This study)

δ¹³Corg [%‰] (Korte and Hesselbo, 2011)

δ¹³Corg [%‰] (Korte and Hesselbo, 2011; Jenkyns et al., 2002)

Late Pliensbachian event

Sinemurian - Pliensbachian boundary event

-2 Myr

-0.6 Myr
FIGURE 8

Robin Hood's Bay (UK) & Portugal

Sinemurian-Plenuschian boundary event (~2 Myr duration)

Plenuschian 87Sr/86Sr versus relative time in the Cleveland (Yorkshire), Wessex (Dorset) and Lusitanian (Porto-Keio) basins

Globoïdlaeulopsis

Dendrogram of the Dolomia Ca [Mg] versus 87Sr/86Sr
<table>
<thead>
<tr>
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<td>Toarcian</td>
<td>tenuicostatum</td>
<td>183.8</td>
<td>+/0.4, estimated uncertainty (radiometric uncertainty)</td>
<td>+0.25</td>
<td>~0.6</td>
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<td></td>
<td></td>
<td>183.8</td>
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<td>~6.3</td>
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<tr>
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<td>spinatum</td>
<td>185.2</td>
<td>+/0.4, extrapolated from above</td>
<td>+0.25</td>
<td>~1.4 (±0.25-0.25)</td>
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<tr>
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<td>margaritatus</td>
<td>187.6</td>
<td>+/0.4, extrapolated from above</td>
<td>0</td>
<td>~2.4 (±0.25)</td>
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<td>davoei</td>
<td>188.0</td>
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<td>+0.15</td>
<td>~2.7 (±0.15)</td>
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<td>+0.15</td>
<td>~9.7 (±0.15-0.25)</td>
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<td>Sinemurian</td>
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<td>Hettangian</td>
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Supplementary Materials

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


[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 slabbened 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 (CaCO₃; 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 S₃MINC and S₅ peaks, resulting from the CO and CO₂ 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 CO₂ fluxes representing the Pyrolysable Carbon (PC: S₁ + S₂ + S₃CO₂) and the Residual Carbon (RC: S₄CO₂ + S₅CO₂). 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...
Reiated 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%. Reated long-term analyses of the TOC content of the IFP160000 standard showed an average concentration of 3.27%, with a StDev 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 CaCO3 analysis (calculated from the mineral carbon content) by Rock Eval was performed on homogenised 1 cm3 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 R2 > 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 CaCO3. 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 CaCO3 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 Moehlas core.

Analysis of δ13C 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 pH levels. Between 1–10 mg of decarbonated sample (aiming for ~25 µg pure carbon) was then weighed into 8×5 mm thin capsules for δ13C TOC analyses. δ13C 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 δ13C values of -43.9‰, -25.1‰ and -22.2‰, respectively, with standard deviations of 0.3‰, 0.2‰ and 0.1‰. Analytical precision for δ13C TOC analyses at the University of Oxford was checked by routine analysis of the Alanine-B international reference standard, which showed average δ13C 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 R² 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 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

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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
~918 m 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 (6.096 m) 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-polymerus 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 2

Ca [%]    TOC [%]

0 10 20 30 40 50

LOWER JURASSIC
Sinemurian
rancostatum

Pliensbachian
jamesoni

Mineral carbon [%]

Hydrogen Index
[mg HC/ g TOC]
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

A. MTM Power Spectrum of the Pliensbachian Calcium Record

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

C. MTM Power Spectrum of the detrended (High-Band Pass Filter) upper rariocostatum to lower margaritatus Calcium Record

D. MTM Power Spectrum of the detrended (High-Band Pass Filter) upper margaritatus to lowermost tenuicostatum Calcium Record
SUPPLEMENTARY FIGURE 5

Fe [high bandpass filter]

Ca [high bandpass filter]
SUPPLEMENTARY FIGURE 6

Fe [bandpass filter]

Ca [bandpass filters]

Relative time (kyr)
SUPPLEMENTARY FIGURE 7