Orbital pacing of the Early Jurassic carbon-cycle and environmental change triggering sapropel formation and seabed methane seepage

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ABSTRACT

The Early Jurassic (~201–174 Ma) was marked by a series of rapid perturbations in climate, the environment and global geochemical cycles, which have been linked to volcanic outgassing and/or the release of biogenic and/or thermogenic methane into the ocean–atmosphere system. Global carbon cycle changes have been documented for the Triassic–Jurassic transition, the Late Sinemurian *Caenisites turneri to Oxynoticeras oxynotum* ammonite Biozones, the Sinemurian–Pliensbachian and the Pliensbachian–Toarcian boundaries and for the Early Toarcian Oceanic Anoxic Event (T-OAE). The state of the global carbon cycle and prevailing climatic and environmental conditions that existed between these major events are, however, poorly constrained. Here, the Lower Sinemurian *Arietites bucklandi* ammonite Biozone at coastal exposures at Kilve, Somerset, UK has been studied. This succession is marked by laminated organic-rich black shales throughout the Bristol Channel Basin and coincides with a 2–3‰ negative carbon-isotope excursion, distinct changes in land vegetation, and blooms of marine prasinophytes (green algae). The event itself does not represent a single perturbation of the regional environment, but follows in a sequence of eccentricity-modulated, precession-paced perturbations that occur throughout the Early Jurassic Hettangian stage, with the periodic formation of organic-rich laminated black shales in the Bristol Channel Basin. However, the Lower Sinemurian event studied herein is more extreme in nature, with sedimentary total-organic-carbon values of 5–11% persisting

over ~100 kyr, possibly in phase with short (~100 kyr) and long (~405 kyr) eccentricity forcing. The formation of methane seep-mounds closely follows the development of laminated black shales. Biogenic methane probably formed in response to microbial methanogenesis in the organic-rich black shale, which was subsequently channeled to the sediment-water interface.

Keywords Early Jurassic, Sinemurian, *bucklandi*, carbon-cycle perturbation, astronomical forcing, methane seepage.

[1] INTRODUCTION

The Early Jurassic (~201–174 Ma) was punctuated by several major and minor perturbations in climate, the palaeoenvironment and global geochemical cycles (Jenkyns *et al*., 2002; Dera *et al*., 2011; Korte and Hesselbo, 2011; Ullmann *et al*., 2014; Brazier *et al*., 2015). The most significant of these perturbations, the Early Toarcian Oceanic Anoxic Event (T-OAE, at ~183Ma) (Jenkyns, 1985, 1988), was characterised by a globally observed negative carbon-isotope excursion (CIE) of up to ~7‰ in marine and terrestrial organic matter and a 3–6‰ negative excursion in coeval carbonate and biomarker compounds (Hesselbo *et al*., 2000, 2007; Jenkyns *et al*., 2002; Kemp *et al*., 2005; Hermoso *et al*., 2009; Schouten *et al*., 2000; Suan *et al*., 2015). This negative shift, which is interposed within an overarching positive excursion, likely resulted from isotopically light carbon input from volcanic outgassing and/or the release of isotopically depleted biogenic or thermogenic methane into the ocean–atmosphere system (Duncan *et al*., 1997; Hesselbo *et al*., 2000; Kemp *et al*., 2005; McElwain *et al*., 2005; Svensen *et al*., 2007; Jenkyns, 2010). Palaeoclimatic and palaeoenvironmental change at this time led to the widespread development of oceanic anoxia and euxinia via elevated nutrient supply, marine primary productivity and water-column stratification (Jenkyns, 2010). Enhanced productivity and preservation of sedimentary organic matter led to increased burial of organic matter in marine and, potentially, lacustrine black shales and caused the overarching positive carbon-isotope excursion due to preferential burial of isotopically light carbon (Jenkyns, 2010). In past years, the T-OAE has been extensively studied and it has now been recognized in both hemispheres (Jenkyns, 1988, 2010; Al-Suwaidi *et al*., 2010). However, several recent studies have demonstrated that the T-OAE was preceded by smaller-magnitude global carbon cycle changes, during the Early Jurassic, in the Late Sinemurian (*Caenisites turneri to Oxynoticeras oxynotum* ammonite Biozones), and at the Sinemurian–Pliensbachian and the Pliensbachian–Toarcian boundaries (Hesselbo *et al*., 2007; Littler et al., 2010; Korte and Hesselbo, 2011; Riding *et al*., 2013).

A 2–3‰ negative CIE in bulk organic matter was previously observed for the Early Sinemurian *A. bucklandi* ammonite Biozone (*Coroniceras rotiforme* ammonite Sub-biozone) at East Quantoxhead (Somerset, UK) (Ruhl *et al*., 2010; Hüsing *et al*., 2014). This negative excursion in $\delta^{13}C_{TOC}$ is associated with an interval of laminated black shale, with elevated total organic carbon (TOC) values of up to ~8%, suggesting (at least) local/basinal change in the depositional environment. The nature of this environmental change and its relation to the global carbon cycle have, however, not been investigated previously. Furthermore, the *A. bucklandi* ammonite zone at Kilve, Somerset, is also marked by methane seepage and the associated formation of large (~1.5m) conical mounds (Cornford, 2003; Allison *et al*., 2008; Price *et al*., 2008). The present contribution addresses (1) a potential Early Sinemurian global carbon cycle perturbation and palaeoenvironmental change leading to black shale deposition in the Bristol Channel Basin, (2) its link to the orbital pacing of Early Jurassic climate and (3) the subsequent genesis of the Early Jurassic seabed methane seepage.

[2] GEOLOGICAL BACKGROUND

[2.1] Origin of sedimentary rhythms and TOC-enrichment in the Blue Lias of Somerset

The Early Jurassic Bristol Channel Basin was part of the Laurasian Seaway, and was marked by a generally progressive marine transgression, including terrestrial to marine transition, during the latest Triassic (Fig. 1; Hesselbo, 2008). The Lower Jurassic Blue Lias Formation formed during a phase of rapid flooding, and resulted in the periodic development of organic-rich laminated black shale (Hallam, 1995, 1997; Warrington *et al*., 2008). The deeper marine (shelf) sediments of the Hettangian and Sinemurian Blue Lias Formation overlie the shallow-marine Lilstock Formation which is Rhaetian (latest Triassic) in age (Cox *et al*., 1999). The *A. bucklandi* ammonite Zone may be marked by a relative sea-level fall, reaching a lowstand in the *C. rotiforme* ammonite Subzone (Hesselbo & Jenkyns, 1998; Hesselbo & Coe, 2000; Hesselbo, 2008).

The Blue Lias Formation has been subject to extensive stratigraphical studies (Hallam, 1987; Smith, 1989; McRoberts and Newton, 1995; Weedon *et al*., 1999; Hesselbo *et al*., 2002; Deconinck *et al*., 2003; Hounslow *et al*., 2004; Mander and Twitchett, 2008; Korte *et al*., 2009; Bonis *et al*., 2010; Clémence *et al*., 2010; Ruhl *et al*., 2010; Bonis and Kürchner, 2012; Hüsing *et al*., 2014). Locally at the North Somerset coast, the Blue Lias Formation defined in Cox *et al*. (1999) has been recognized as Aldergrove Beds, St. Audrie's Shales, Blue Lias, Kilve Shales, Quantocks Beds, Doniford Shales and Helwell Marls (Palmer, 1972). This major lithostratigraphical unit with regional extent comprises alternations of limestones and marls/ shales on the Somerset coast (Ruhl *et al*., 2010). Limestone beds (10–20 cm thick, occasionally up to 50 cm thick) are mostly micrite mudstones to wackestones. The limestone beds are fine-grained, containing varying proportions of clay minerals and micrite (Paul *et al*., 2008), which are suggested to have settled from suspension (Weedon, 1986). Some limestone beds are also clearly concretionary (Hallam, 1986; Weedon, 1986). The limestone beds of the Blue Lias Formation alternate with grey marls and organic-rich laminated black-shales (Campos and Hallam, 1979; Hallam, 1986; Paul *et al*., 2008), which variably contain terrigenous clay minerals and marine- and terrestrially-derived organic matter (Weedon 1986; Clémence *et al*., 2010). The sedimentary rhythms in the Blue Lias Formation consist of a laminated black-shale grading into marl, commonly with concretionary to tabular micritic limestone, which has been suggested to be diagenetic in origin (Paul *et al*., 2008). These sedimentary rhythms are not always symmetrical because organic-rich shale or marl/limestone beds were not always developed, or because the carbonate-rich sediments have been diagenetically altered (Ruhl *et al*., 2010). The origin of cyclic sedimentation in the Blue Lias Formation was discussed by Campos and Hallam (1979), Weedon (1986), Hallam

(1986), Bottrell and Raiswell (1989), Smith (1989) and Paul *et al.* (2008).

The geographical extent of the limestone-shale couplets indicates chronostratigraphical significance and hence a stable allogenic forcing mechanism likely to be high-frequency climate control (Weedon, 1986; Smith, 1989). Integrated stratigraphical and palaeomagnetic studies on the Blue Lias Formation of Somerset demonstrate that the sedimentary rhythms, with the periodic formation of laminated organic-rich black shale, directly reflect orbitally controlled changes in the depositional environment at ~20 kyr precession periodicities, modulated by the short and long eccentricity cycles (Ruhl *et al.*, 2010; Bonis *et al.*, 2010; Hüsing *et al.*, 2014). Periodically enhanced TOC values in the Hettangian and the Lower-most Sinemurian Blue Lias Formation, with values of up to 10%, are especially elevated at the base *P. planorbis* ammonite zone, middle *A. liasicus* ammonite zone and *S. angulata–A. bucklandi* ammonite zone boundary, probably in response to 405 kyr (and potentially ~2 Myr) modulated, precession-controlled changes in the palaeo-depositional environment (Ruhl *et al.*, 2010; Hüsing *et al.*, 2014; Sha *et al.*, 2015).

Black shales from the bucklandi zone at Kilve have previously been categorized as oil shale, albeit from rather low quality (Gallois, 1979). A 2 m thick black-shale interval, with TOC >10%, in the *A. bucklandi* ammonite Zone in East Quantoxhead, is marked by a ~ 2.5‰ negative excursion in $\delta^{13}C_{TOC}$ (Ruhl *et al.*, 2010). Earlier 1–2‰ fluctuations in $\delta^{13}C_{TOC}$ in the Hettangian and the Sinemurian succession of St Audries Bay and East Quantoxhead in Somerset potentially reflect changes in the global exogenic carbon cycle, on Milankovitch periodicities (Clémence *et al.*, 2010; Ruhl *et al.*, 2010; Hüsing *et al.*, 2014). Alternatively, these periodic alternations in $\delta^{13}C$ may express changes in sedimentary organic-matter source, changes in the magnitude of marine and/or terrestrial fractionation for ^{12}C, and/or changes in the basinal isotopic composition of the dissolved inorganic carbon pool in response to changes in basin hydrography. The orbitally-paced deposition of laminated black shale at this time was probably in response to changes in both productivity and preservation. This was possibly due to enhanced nutrient (and terrestrial organic-matter) supply and water-column stratification resulting from precession-controlled changes in the hydrological cycle modulated by eccentricity (Bonis *et al.*, 2010; Clémence *et al.*, 2010; Ruhl *et al.*, 2010). The Kilve coastal cliff section studied here is located west of Bridgwater and the River Parrett on the Somerset coast, UK, ~500 m east of Kilve Beach and ~1 km north of Kilve village (Fig. 1). The exposure covers the stratigraphical interval of the *bucklandi* ammonite zone with laminated black shales (with TOC up to ~10%), as in East Quantoxhead (Fig. 2). The foreshore outcrop is also marked by conical seep-mounds occurring at a single stratigraphical level, that overlies this high TOC black shale interval by ~5 m (Figs 2, 3 and 4) (Whittaker and Green, 1983; Cornford, 2003; Allison *et al.*, 2008; Price *et al.*, 2008). The cliff-section sampled in the present study is ~50 m west of the nearest visible seep-mound on the foreshore.

[2.2] **Early Jurassic chronostratigraphy**

The age of the Triassic–Jurassic boundary is radiometrically constrained at 201.36 ± 0.17 Ma in the Pucara Basin, Peru (Schaltegger *et al.*, 2008; Schoene *et al.*, 2010; Wotzlaw *et al.*, 2014) and astrochronologically constrained at 201.42 ± 0.022 Ma in the Newark/Hartford Basins, USA (Blackburn *et al.*, 2013) (Fig. 5). The duration of the Hettangian Stage has previously been estimated using cyclostratigraphy at > ~1.29 Myr, from the relatively incomplete marine Blue Lias Formation succession in Dorset and Devon, southwest England, or at ~2.86 Myr based on an assumed constant linear Early Jurassic decrease in seawater $^{87}Sr/^{86}Sr$ ratios (Weedon *et al.*, 1999). More recent estimates 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 in 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 base Sinemurian in the Pucara Basin of Peru (Schaltegger *et al.*, 2008; Guex *et al.*, 2012). The integrated bio-, magneto- and cyclostratigraphic framework for the Lower Jurassic Blue Lias Formation, combined with radiometric dating, directly constrains the age and duration of changes in the depositional environment in the Early Jurassic Bristol Channel Basin.

[2.3] **Lower Sinemurian methane seeps**

Several large, conical mounds have been observed in a foreshore outcrop east of Kilve Beach in western Somerset, occurring at a discrete level within the Kilve Shales (Palmer, 1972) in the *C. rotiforme* ammonite Subzone of the *A. bucklandi* ammonite Zone (Whittaker and Green, 1983; Cornford, 2003; Allison *et al*., 2008; Price *et al*., 2008). These mounds are up to 1 m high and up to 3 m in diameter and their flanks are formed by a limestone shell, which is composed of micritic carbonate and includes pods and sheets of bioclasts and intraclasts (Allison *et al*., 2008). The shape of ammonites and intraclasts on the flanks of the mounds suggests cementation close to the sediment–water interface, prior to compaction (Allison *et al*., 2008). This mound-forming level is interpreted as being largely oxygen-deficient because of the sparse presence of benthic biota, except for one of the mounds, where benthic foraminifera (*Involutina liassica)*, bivalves, crinoidal fragments and gastropods, are present (Allison *et al*., 2008; Price *et al*., 2008). The abundance of the benthic foraminifera *Involutina liassica* in one mound indicates at least brief oxygenation (Allison *et al*., 2008; Price *et al*., 2008). The mound-forming authigenic carbonate (cf. Liang et al., 2016) has depleted carbon-isotope signatures of -11.5 ‰ to -32.3 ‰ and such ^{12}C-enriched signature has been interpreted to originate from anaerobic methane oxidation, and mixing of the liberated carbon with seawater-dissolved inorganic carbon (Allison *et al*., 2008; Price *et al*., 2008).

Early Jurassic seep mounds have previously been observed in several localities in Europe, including an Upper Pliensbachian outcrop in southern France (van de Schootbrugge *et al.*, 2010), and a Lower Toarcian coastal Jet Rock outcrop at Ravenscar, Yorkshire, UK (Fig. 4; Hesselbo *et al*., 2013). The shape and lithological composition of the conical mounds at Ravenscar are quite similar to the ones on the foreshore of the Kilve coast.

[3] MATERIALS AND METHODS

[3.1] **MATERIALS**

[3.1.1] **The Early Sinemurian *A. bucklandi* zone at Kilve**

In this study, 15.6 m of mudstone and laminated black shale of the Early Sinemurian *A. bucklandi* ammonite biozone (*rotiforme* subzone) was sampled at 10–11cm resolution at the coastal cliff outcrop east of Kilve Beach (Figs 3 and 4; 51°11'39.4"N, 3°13'00.8"W). The logged and sampled interval starts at the top of the Blue Lias and covers most of the Kilve Shales (following Palmer's division; Palmer, 1972), both of which belong to the Blue Lias Formation (Cox *et al.*, 1999). The sampled interval is stratigraphically coeval with the 2–3‰ negative CIE as observed in the middle of the *A. bucklandi* ammonite zone at East Quantoxhead and it also spans the stratigraphic horizon with methane seep occurrence, ~5 m above laminated black shales (Fig. 2; Ruhl *et al.*, 2010). In the cliff section, samples were only collected from the grey mudstones and the laminated black-shales and not from the occasional (concretionary) limestone beds.

The base of the sampled outcrop, which is close to the base of the Kilve Shales, is marked by alternations of limestones and marly mudstones containing (complete and fragments of) macrofossils, including ammonites, bivalves and crinoids (Figs 3 and 4). There is a ~2 m thick (Figs 3 and 4), laminated black shale with little bioturbation and few ammonite fossils at stratigraphical height of 3.7–5.5 m. The trace fossil *Diplocraterion* appears close to the top of the black-shale interval (Figs 3 and 4).

Sediments overlying the laminated black-shale interval consist of alternating marl and shale beds, with a few discrete nodular limestone beds. This interval has yielded ammonites, bivalves and crinoids. Coalified wood fragments of up to 10 cm long occur throughout, especially in the black shales (Figs 3 and 4).

[3.1.2] **Early Toarcian conical seep mounds at Ravenscar**

Conical seep mounds in the Lower Toarcian Upper Jet Rock at Ravenscar (Yorkshire; 54°24'28''N, 0°27'34''W) succeed the high TOC (~15%) Lower Jet Rock by ~3 m (Hesselbo et al., 2013). Samples were collected from several carbonate mounds on the foreshore for carbon and oxygen isotope analysis in order to test the origin of the seep formation during sub-seafloor gas venting (Fig. 4).

[3.2] **METHODS**

Total Carbon (TC) and Total Inorganic Carbon (TIC) were determined for all the studied samples using a Strohlein Coulomat 702 Analyser at the Department of Earth Sciences, University of Oxford. For TIC analyses, ~120 mg of powdered sample was roasted overnight at 420 °C to remove the organic matter. Total carbon (~80 mg of powdered sample) and TIC were measured, respectively, on the unroasted and roasted samples, and TOC was the difference between the two. Reproducibility of sample analyses with this method is generally better than 0.1% (Jenkyns 1988). The in-house SAB134 (Blue Lias organic-rich marl) standard were regularly measured. The long-term average value and standard deviation of TOC measurements on the in-house SAB134 standard is 2.95% and 0.069%, respectively. Organic matter was further characterized by Rock-Eval pyrolysis on a Rock-Eval VI standard instrument with pyrolysis and oxidation ovens, providing Hydrogen Index, Mineral Carbon, Oxygen Index, Residual Organic Carbon, Tmax and TOC. Laboratory procedures as described in Behar *et al.* (2001) were used and the measurements performed at the Department of Earth Sciences, University of Oxford. Quality control was provided by the in-house SAB134 standard, which is homogenized Blue Lias organic-rich marl, and the certified IFP160000 standards, which were regularly run between samples. The standard deviation on TOC and HI analyses of the in-house SAB134 and the reference IFP160000 standards is, respectively, 0.07 and 0.07 % (TOC) and 22.7 and 10.6 mg HC/ gTOC (HI).
The analyses of $\delta^{13}C_{TOC}$ was performed on one gram of homogenized sample that was treated with 40 mL cold HCl (3 molar) to dissolve the carbonate. Samples (dissolved in 3 molar HCl) were then put on a hot plate for 2 hours at 60°C. They were subsequently rinsed 4 times with distilled water to reach neutral pH. About 1–15 mg, depending on TOC concentration, of oven-dried and powdered decarbonated sample residue was weighed into 8×5 mm tin capsules for $\delta^{13}C_{TOC}$ analyses. These analyses were performed on a Sercon Europa EA-GSL

sample converter connected to a Sercon 20-22 stable isotope ratio mass-spectrometer running in continuous flow mode with a helium carrier gas with a flow rate of 70 ml/min. Carbon-isotope ratios were measured against an internal alanine standard ($\delta^{13}C_{alanine}$ = –26.9‰ ± 0.2‰ V-PDB [Vienna Peedee belemnite]) using a single-point calibration, at the Research Laboratory for Archaeology and History of Art (RLAHA), University of Oxford, UK. The in-house (RLAHA) alanine standard is regularly (weekly) checked against the certified USGS40, USGS41, and IAEA-CH-6 international reference standards, with a long-term average alanine $\delta^{13}C$ value of -26.92‰ and a standard deviation of 0.15‰.

$\delta^{13}C_{carb}$ analyses were performed at the Stable Isotope Laboratory at the Open University, Milton Keynes, UK. Bulk samples were dissolved in phosphoric acid on a Thermo Gas Bench II, and C and O isotope analysis was performed on a Thermo Finnegan Delta+ Advantage mass spectrometer. Carbon- and oxygen-isotopic compositions were expressed relative to VPDB by reference to in-house carbonate standards calibrated to NBS-19. Reproducibility is ±0.1 ‰ for O and < 0.1 ‰ for C.

Standard palynological techniques (Wood *et al.*, 1996) were used, and sample preparation was carried out at the National Oceanographic Centre, University of Southampton, UK. The samples were rough-crushed and then subjected to successive treatments in concentrated HCl (30%) and HF (60%) with both treatments being followed by rinsing of the sample with deionized water to neutral pH. Following the HF treatment, the samples were sieved at 15 µm. This process was followed by a short treatment in hot concentrated HCl to solubilize any neoformed fluorides. The samples were then diluted with 500 ml of water and sieved again at 15 µm. The resulting kerogen concentrate was stored in vials, and strew slides were mounted in Elvacite 2044.

[4] RESULTS

[4.1] **Early Sinemurian $\delta^{13}C$ and kerogen characterization at Kilve**

The TOC content in the studied successions is generally between 1–3%, but increases up to 10.9% in the organic-rich laminated black-shale interval at the lower part of the succession.

Total Organic Carbon values are also elevated at discrete horizons at ~ 3, ~ 6.5, ~ 10.8 and ~ 12.9 m in the cliff section at Kilve (Fig. 3). High-resolution carbon-isotope analyses of bulk-rock samples, from ~ 4 m below the black-shale interval up to 4.5 m above the methane seep horizon, show a distinct 3‰ negative excursion in $\delta^{13}C_{TOC}$ and a 2‰ negative excursion in $\delta^{13}C_{carb}$ (Fig. 3). The $\delta^{13}C_{TOC}$ negative shift is similar in magnitude to the one previously observed in coeval strata of nearby East Quantoxhead (Ruhl *et al*., 2010). The depleted $\delta^{13}C_{TOC}$ directly coincides with elevated TOC values in the laminated black-shale interval; $\delta^{13}C_{carb}$ values remain, however, low for another ~1.5 m, with TOC concentrations already restored to background values (Fig. 3). Hydrogen Indices from Rock Eval pyrolysis vary between 108 and 720 mg HC/ gTOC, with consistently elevated values in the laminated black-shale interval (Fig. 3). Elevated HI values closely match elevated TOC in the lower part of the section (up to 7 m), but this correlation breaks down in the upper part of the studied interval (Fig. 3). Tmax values of 428–440°C suggest an immature to early mature kerogen in the studied succession (Supplementary Table 1). The characterization of kerogen type, defined by both HI and Tmax values of the studied samples, suggests a gradual transition of kerogen Type II, to Type I and back to Type II/III passing up-section (Fig. 3). This stratigraphical evolution suggests distinct changes in the composition of the sedimentary organic matter in the relative proportions of marine phytoplankton and terrestrial higher-plant organic matter. The bulk-rock $\delta^{13}C_{carb}$ record of the Lower Sinemurian at Kilve, geographically ~ 50 m away from the nearest visible conical seep-mound (although mounds may be hidden in the cliff near the sampled section), also exhibits a shift to relatively depleted values right at the level of the seep-mounds (Fig. 3).

[4.2] δ^{13}C analyses of Early Toarcian conical seep mounds at Ravenscar

The previously published isotopic analyses of bulk-rock samples of the Lower Sinemurian seep-mounds at Kilve show relatively depleted values for both carbon and oxygen ($\delta^{13}C_{carb}$: 0 to –32‰; $\delta^{18}O_{carb}$: –3 to –11‰; Fig. 4; Allison *et al*., 2008; Price *et al*., 2008). The isotopic analyses of bulk-rock samples of the Lower Toarcian seep-mounds at Ravenscar (Yorkshire, UK) reported here also show relatively depleted values for both carbon and oxygen ($\delta^{13}C_{carb}$: –6 to –18‰; $\delta^{18}O_{carb}$: –10 to –14‰; Fig. 4).

[4.3] **Palynomorph and kerogen assemblages**

Samples studied for palynomorphs and kerogen are generally strongly enriched in amorphous organic matter (AOM), which is typical for black shales, and the palynomorph diversity is relatively low (Fig. 3). The percentage AOM relative to total kerogen (% AOM/total kerogen) is especially high (up to 80%) in the black-shale interval, where wood accounts for only 8% of the total kerogen (Fig. 3, Supplementary Table 2). Fern spores are generally low in abundance, whereas the gymnosperm pollen species *Classopollis meyeriana* is consistently superabundant, accounting for more than 88% of the total terrestrial palynomorph composition (Fig. 3). The *Classopollis meyeriana* abundance increases to almost 100% of the terrestrial palynomorph fraction in the laminated black-shale interval (Fig. 3). A subsequent change in palynofacies is observed from 6.15 m upwards, where the palynomorph composition becomes more diverse, with the presence of acritarch genus *Micrhystridium*; the amount of wood fragments also increases (Fig. 3; Supplementary Table 2). By contrast, palynomorph diversity is much lower, AOM content is higher, and the prasinophyte (green algae) genus *Tasmanites* dominates the microplankton in the laminated black-shale interval with depleted $\delta^{13}C$ values (Fig. 3; Supplementary Table 2).

The relative abundance of *Tasmanites*, relative to the total microplankton assemblage, gradually decreases from 100% at the top of the laminated black-shale interval to ~16% at the top of the studied section (Fig. 3). The percentage of marine palynomorphs relative to the total palynomorph assemblage (marine + terrestrial palynomorphs) is generally low (<13.4%), and is especially low in the laminated black-shale interval (Fig. 3).

[5] DISCUSSION

[5.1] **The Early Sinemurian $\delta^{13}C$ record and orbital pacing of palaeoclimate and the palaeoenvironment**

The observed ~3‰ negative excursion in $\delta^{13}C_{TOC}$ at Kilve (Fig. 3) stratigraphically coincides with a similarly sized negative CIE at East Quantoxhead (Fig. 2; Ruhl *et al*., 2010). The contemporaneous ~2‰ negative excursion in $\delta^{13}C_{carb}$ at Kilve (Fig. 3), may reflect changes in the carbon-isotopic composition of Early Sinemurian seawater dissolved inorganic carbon (DIC) in the Bristol Channel Basin. Combined, these data may suggest a change in the isotopic composition of the globally exchangeable carbon pools. Similarly, the observed sedimentary carbon-isotope fluctuations throughout the Early Jurassic Hettangian stage in the marine sediments of the Bristol Channel Basin (Hesselbo *et al*., 2002; Clémence *et al*., 2010; Ruhl *et al*., 2010), may also have reflected true changes in the global exogenic carbon cycle because equally sized and spaced carbon-isotope fluctuations are also observed in the sedimentary organic matter of the continental Newark and Hartford Basin in the eastern USA (Whiteside *et al*., 2010). Alternatively, periodic changes in the source of the sedimentary organic matter (explaining varying $\delta^{13}C_{TOC}$) and/or periodic changes in the water-column redox state may have taken place, with the oxidation of sedimentary organic matter and the release and subsequent biomineralization of ^{12}C during phases of re-oxygenation (explaining varying $\delta^{13}C_{carb}$) (Clémence *et al*., 2010; Ruhl *et al*., 2010).

The $\delta^{13}C_{carb}$ record at Kilve remains low (for another ~1.5 m) following the recovery of the $\delta^{13}C_{TOC}$ signal (Fig. 3). Sedimentary organic-matter content in lime- and mudstone stratigraphically succeeding the organic-rich black shales is likely to have been partly recycled and of a mixed marine/terrestrial origin, resulting in partly elevated HI values (Fig. 3). The organic-rich laminated black shale was probably deposited under anoxic (or euxinic) conditions, given the lack of bioturbation. The preceding and overlying mudrocks are strongly bioturbated, and the trace fossil *Diplocraterion* reappears at the top of the black shale interval (Fig. 3). The switch to re-oxygenated conditions following the deposition of the organic-rich black shale, may have oxidized and remobilized the ^{12}C enriched organic carbon (Clémence *et al*., 2010). Degradation of the sedimentary organic matter and the subsequent release of isotopically light (^{12}C) carbon into the dissolved inorganic carbon pool of pore-spaces and the overlying seawater DIC pool allowed the precipitation of isotopically depleted (diagenetic) carbonate, following the deposition of organic-rich black shale. Alternatively, anaerobic oxidation of methane under anoxic/ euxinic conditions in the sedimentary pore space during deposition of the organic-rich black shale may have significantly decreased the carbon-isotope composition of interstitial fluids and the overlying water-column. Such a process may also have allowed cementation at the seabed or in the shallow subsurface, during deposition of the organic-lean mudrocks following the formation of the organic-rich black shale.

Irrespective of the true cause of carbon-isotope changes in the Lower Jurassic sedimentary records of the Bristol Channel Basin, the observed fluctuations in biota, lithology, sedimentary organic matter, TOC and $\delta^{13}C$ are periodic in nature and likely reflect high-frequency climatic and environmental change at Milankovitch periodicities (Bonis *et al.*, 2010; Clémence *et al.*, 2010; Ruhl *et al.*, 2010; Whiteside *et al.*, 2010; Hüsing *et al.*, 2014; Sha *et al.*, 2015). The Lower Sinemurian *C. rotiforme* ammonite Subzone was previously suggested to coincide with a sea-level lowstand (Hesselbo, 2008). The laminated black shales in the Bristol Channel Basin of *rotiforme*-Subzone age, however, formed directly in line with eccentricity modulated, precession-controlled laminated black shales throughout the Hettangian and the Lower Sinemurian, suggesting continued higher-order astronomical control on the depositional environment rather than only a temporary sea-level change (Ruhl *et al.*, 2010; Hüsing *et al.*, 2014). The laminated black shale of the *C. rotiforme* Subzone studied here, is, however, arguably more expanded and more organic-rich compared to preceding Upper Hettangian and Lower Sinemurian strata (Fig. 2).

The periodic occurrence of highly elevated TOC enrichments in Plio- and Pleistocene sapropels in the Eastern Mediterranean are strongly paced by eccentricity modulated precession forcing and the development of anoxic bottom water conditions in response to regional changes in run-off (Hilgen, 1991; Calvert and Fontugne, 2001; Lourens *et al.*, 2004; Becker et al., 2005; Bosmans et al., 2015).

Palaeocene and Eocene hyperthermals are marked by distinct changes in the global carbon cycle, with major repercussions for the global climate and palaeoenvironment, and they have been recognized to be paced at orbital timescales (Lourens *et al.*, 2005; Zachos *et al.*, 2010).

The Eocene Thermal Maxima 2 and 3 (ETM2 and ETM3) occur during short and long-term eccentricity maxima and possibly even at longer (~1.2 Myr) periodicity maxima, whereas the pacing of ETM1 (at the Palaeocene-Eocene boundary) is slightly out of phase, possibly due to non-orbital internal forcing of the Earth system (Zachos, *et al.*, 2010).

The observed Early Jurassic Hettangian and Sinemurian periodic formation of laminated black shales and coeval fluctuations in $\delta^{13}C$ and palaeoenvironmental proxies (e.g. TOC, magnetic susceptibility, $CaCO_3$, biological proxies) in the Bristol Channel Basin are also paced at orbital time-scales (Figs 2, 5 and 6; Bonis *et al.*, 2010; Clémence *et al.*, 2010; Ruhl *et al.*, 2010; Hüsing *et al.*, 2014). They likely reflect intensified, regional to global, environmental change on short astronomical (precession) time-scales, modulated by short- (~100 kyr) and long-term (~405 kyr) (and possibly even longer ~2 Myr) eccentricity (Figs 2 and 6; Ruhl *et al.*, 2010; Hüsing *et al.*, 2014; Sha *et al.*, 2015), coeval with eccentricity modulated precession and obliquity forcing in the continental Newark (eastern USA) and Jungar (northwestern China) Basins (Kent and Olsen, 2008; Sha et al., 2015), and also similar to Plio- and Pleistocene conditions in the Eastern Mediterranean and possibly also during the Eocene hyperthermals.

Periodic palaeoenvironmental and palaeoceanographical changes in the Early Jurassic of the Bristol Channel Basin are relatively minor compared with the Triassic–Jurassic and the Early Toarcian oceanographical changes. These are both more intense and longer in duration (Suan *et al.*, 2008; Deenen *et al.*, 2010; Ruhl *et al.*, 2010; Kemp *et al.*, 2011; Huang and Hesselbo, 2014; Boulila *et al.*, 2014). Similar to the ETM1, at the Palaeocene-Eocene boundary, these events were suggested to have resulted from internal (i.e. volcanic) forcing of the Earth system (Hesselbo *et al.*, 2002; Deenen *et al.*, 2010; Jenkyns, 2010; Ruhl *et al.*, 2011; Sell *et al.*, 2014; Percival *et al.*, 2015). Studying the time-periods between such major events allows for better constraints on the background sensitivity of the Earth system, and our data suggest that major changes in the palaeoenvironment and basin oceanography did occur over orbital timescales, in a warm, largely ice-free, world.

[5.2] **Early Sinemurian climatic and environmental change**

Elevated TOC contents of up to 10% in the Lower Sinemurian laminated black shale interval studied here coincide with high HI values (>700 mg HC/ gTOC) (Fig. 3) and increased levels of amorphous organic matter. This Type I kerogen may have been sourced by bacterially degraded marine algal organic matter (Fig. 3). Alternatively, lipid remains of leaf waxes may have been the source of this kerogen type with high HI values (Wignall, 1994; Tyson, 1995; Killops and Killops, 2005). The end-Triassic mass extinction interval in the Eiberg Basin of Austria is marked by strongly enhanced HI values, coinciding with abundant *Classopollis meyeriana* pollen (Ruhl *et al.*, 2010). Similarly, the typical Type I/II kerogen observed in the Lower Sinemurian black-shale interval at Kilve, also coincides with a shift to almost 100% *Classopollis meyeriana* in terms of the total terrestrial palynomorph assemblage (Fig. 3). The superabundance of the thermophilic *Classopollis* pollen during this interval, suggests a shift to even warmer climatic conditions from an already super-greenhouse state in the Hettangian (Bonis *et al.*, 2010; Bonis and Kurschner, 2012; Riding *et al.*, 2013). Possible astronomically-controlled changes in the hydrological cycle during this warm phase in the earliest Jurassic (Hettangian), together with the supply of terrestrial organic matter to the basin, may have significantly affected the marine palaeoenvironment (Bonis *et al.*, 2010). Alternatively, the enhanced supply of terrestrial organic matter may have resulted from an approaching palaeocoastline during an Early Sinemurian sea-level lowstand (Hesselbo, 2008). The bloom of the *Tasmanites* green algae (a "disaster index") during the Early Sinemurian negative perturbation in $\delta^{13}C$, similar to that following the end-Triassic mass extinction in the Bristol Channel and the west Germanic Basin (van de Schootbrugge *et al.*, 2007; Richoz *et al.*, 2012), suggests a salinity- and/or temperature-stressed environment in the marine realm at this time (Vigran *et al.*, 2008). The change in the sedimentary organic matter type, combined with the change in apparent redox state of waters in the Bristol Channel Basin during the time-interval studied, could potentially explain the observed changes in the organic and inorganic $\delta^{13}C$ values. Whether the negative CIE is a local (kerogen source-related or diagenetic) phenomenon, or represents global carbon-cycle change remains to be tested in other basins or by the sampling of specific carbon pools. The changes in sedimentary geochemistry and organic matter do, however, suggest changes in climate and the terrestrial and marine palaeoenvironment, likely at orbital time-scales.

[5.3] **Methane seepage linked to organic-rich shale formation**

Marine methane seepage and the formation of authigenic carbonates in/on the seabed have occurred before and throughout the Phanerozoic, in a wide variety of environments and with many different (shallow and deep) sources for the bio-/ thermogenic methane (Tryon *et al.*, 2002; Jiang *et al.*, 2003; Niemann *et al.*, 2006; Walter Anthony *et al.*, 2012; Kiel *et al.*, 2013; Nesbitt *et al.*, 2013; Skarke *et al.*, 2014). One of the best-studied Jurassic methane seeps formed in Oxfordian times (~160 Ma) at Beauvoisin, southeast France (Peckmann *et al.*, 1999). Highly depleted $\delta^{13}C$ values of down to -30 ‰ in calcite nodules within the section studied, likely result from hydrocarbon sourced methane seepage (Louis-Schmid *et al.*, 2007). Conical seep-mounds formed on the seabed during deposition of the Lower Sinemurian *A. bucklandi* ammonite Biozone (*C. rotiforme* ammonite subiozone) succession, now occur ~5 m stratigraphically above the top of the laminated black shale interval and crop out on the fore-shore at Kilve. Previous analyses of these conical mounds indicate that they were likely formed as seafloor mud volcanoes associated with methane seepage (Allison *et al.*, 2008; Price *et al.*, 2008). Micritic carbonates of the flanks of the mounds typically show strongly depleted $\delta^{13}C_{carb}$ values of 0 to –32‰, which likely resulted from microbial anaerobic methanotrophy and subsurface methanogenesis (Allison *et al.*, 2008; Price *et al.*, 2008). The isotopic compositions of coeval mudrocks adjacent to the seep-mounds are generally less depleted in $\delta^{13}C_{carb}$, but still display values of down to –20‰ (Allison *et al.*, 2008). The coeval stratigraphical level in the cliff-section studied here, ~ 50 m away from the nearest visible mound on the foreshore, also shows an abrupt shift towards more depleted $\delta^{13}C_{carb}$ values (from +1 to –0.5‰). This possibly suggests that methane-seepage from the mud-mounds actively altered the isotopic composition of the nearby DIC pool during oxidation of methane at the seabed (Fig. 3; Aloisi et al., 2000). The $\delta^{13}C_{TOC}$ record from the same cliff section, however, does not show a coeval shift to more depleted values and sedimentary organic matter at this stratigraphical interval. This is continuously terrestrially-dominated, with low HI values of 200 mg HC/ gTOC and relatively sparse (6%) marine palynomorphs (Fig. 3). Therefore, methane seepage from the seafloor was likely localized and concentrated at the seep-mounds, with its oxidation mostly at and around the mounds and with limited dispersion into the surrounding water-column and atmosphere.

The nature and source of the methane seeping at the early Sinemurian seafloor has been suggested to have been biogenic in origin, deriving from Triassic rocks (Cornford, 2003) or the directly underlying organic-rich Kilve Shales (Allison *et al*., 2008). Alternatively, the methane had a thermogenic origin and was derived from Palaeozoic rocks in the deep subsurface (Price *et al*., 2008). The latter model would suggest a migration of methane-gas along deep fault systems, to the surface (Cornford, 2003). The seep-mounds are, however, randomly located on the foreshore, and do not show any clear alignment along observable fault systems.

Here, we propose a model (Fig. 7) suggesting biogenic methane sourced from the underlying Lower Sinemurian, *A. bucklandi* ammonite Biozone, laminated organic-rich black shale. This is within the Kilve shales following Palmer (1972). In this model, organic-lean mudstones from the Lower Sinemurian *A. bucklandi* ammonite Biozone formed under oxygenated seafloor conditions, due to limited marine and terrestrial sedimentary organic-matter supply and preservation (Phase 1, Fig. 7). Oxygenated conditions in the pore waters and minor microbial methanogenesis instigated only a minor flux of gaseous methane across the sediment–water interface and into the overlying water-column. Environmental and palaeoceanographical changes in response to orbitally-paced changes in climate and palaeoenvironment may have enhanced the hydrological cycle, leading to an increased flux of terrestrial organic matter into the basin (Phase 2, Fig. 7; Fig. 3). Enhanced nutrient supply possibly also initiated increased marine primary productivity. This larger flux of carbon to the sedimentary organic matter pool, together with possible density stratification of the water-column resulting from increased run-off, initiated a switch to anoxic conditions in the sedimentary pore waters and possibly also the overlying water-column. The increased flux of organic carbon, combined with enhanced preservation under anoxic conditions, ultimately resulted in the formation of the laminated organic-rich black shales, with TOC >10 % (Fig. 3). Anoxic conditions in the sedimentary pore space may have initiated microbial methanogenesis with a strongly enhanced flux of methane to the sediment-water interface, similar to modern-day anoxic/organic-rich lake-beds or in the modern-day Black Sea (Mazzini *et al.*, 2004; Niemann *et al.*, 2006). A subsequent transition back to earlier palaeoclimatic and palaeoenvironmental conditions returned the system to organic-lean mudrock deposition (Phase 3, Fig. 7; Fig. 3). An elevated flux of biogenic methane from the underlying organic-rich laminated shale, however, still reached the sediment-water interface under conditions of elevated methane pore pressure and a non-compacted/ non-cemented open pore space in the overlying organic-lean mudrock. Continued burial of the laminated organic-rich shale and the initiation of compaction and/or cementation of the host-rock likely prohibited biogenic methane from reaching the sediment-water interface through random dispersion through the pore spaces of the overlying mudrock (Phase 4, Fig. 7). Overpressured free methane in the organic-rich host-rock probably migrated upwards, possibly along faults that initiated, for example, due to compaction-related failure (Cornford, 2013; Talukder, 2012). The channeling of free biogenic methane from the organic-rich black shale interval to the sediment-water interface along these faults, which possibly developed also into conduits, likely resulted in highly localized methane release from the seabed into the overlying water-column, allowing seep mounds to form. Such a model directly explain the observations made within the Lower Sinemurian succession at Kilve.

Interestingly, similar observations were made for the Lower Toarcian succession at Ravenscar Yorkshire, UK (Hesselbo *et al*., 2013). Methane-seep carbonates, also with depleted $\delta^{13}C_{carb}$ values of –6 to –18‰, occur ~3 m stratigraphically above the most organic-rich interval (up to 19% TOC) in the Lower Toarcian organic-rich Jet Rock (Mulgrave Shale Member; Figs 4 and 8; Hesselbo *et al*., 2013; Kemp *et al.*, 2011). Also there, the seeps were not directly linked to nearby faults. The sedimentary organic matter in the Jet Rock at Port Mulgrave was dominantly sourced by marine algae deposited under anoxic to euxinic conditions (Salen *et al.*, 2000, French *et al*., 2014). Differences in the stratigraphical distance between the top of the organic-rich black-shale interval and the subsequent occurrence of methane seep-mounds in the Lower Sinemurian of Somerset (~5 m) and the Lower Toarcian of Yorkshire (~3 m), may reflect differences in lithology and original pore space. This may also reflect different compaction rates or differences in water-depth and/or sedimentary TOC content, potentially leading to differences in the build-up of over-pressure in the sediment pile. With the model proposed here, formation of seabed methane seep-mounds would probably occur in a limited stratigraphical window after the deposition of an organic-rich black shale: after sufficient compaction and the formation of subsurface structures (i.e. faults) for the channelling of free methane, but before complete closure by compaction or cementation of the interstitial pore-spaces.

[6] CONCLUSIONS

Changes in the isotopic composition of organic and inorganic sedimentary carbon from the Lower Sinemurian (*A. bucklandi* ammonite Biozone) sedimentary record at Kilve, Somerset, UK in the Bristol Channel Basin coincided with changes in the depositional environment and palaeoclimate. The 3‰ negative excursion in the $\delta^{13}C_{TOC}$ and the 2‰ negative excursion in the $\delta^{13}C_{carb}$, together with a bloom of *Tasmanites* (green algae) and an apparent shift to anoxic/euxinic water-column conditions, with the deposition of organic-rich laminated black shales. These phenomena, combined with a change in the terrestrial vegetation assemblage, occurred over a period of ~100 kyr. This perturbation of the palaeoenvironment was possibly in phase with a short (~100 kyr) and long-term (~405 kyr) eccentricity maximum and succeeds similar, but less intense, events throughout the earliest Jurassic (Hettangian) in the Bristol Channel Basin.

The formation of methane seep-mounds on the Lower Sinemurian (*A. bucklandi* ammonite Biozone) seabed in the Kilve area followed the deposition of organic-rich laminated black shale deposition by ~200 kyr (~5 m). Seep formation possibly resulted from biogenic methane production by microbial methanogenesis in the organic-rich shale and the channelling of this gas, which was likely over-pressured in the pore spaces of the source-rock, along factures and faults to the sediment-water interface. Similar observations, with methane seep-mounds overlying the Lower Toarcian organic-rich Jet Rock at Ravenscar, Yorkshire, suggests that seabed seep-mound formations may be a common phenomenon in the stratigraphical record, following local, regional or global black-shale deposition.

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FIGURE CAPTIONS

Fig. 1. Geographic maps. (A) Early Jurassic global palaeogeography, modified after Dera *et al*. (2011) and Korte *et al*. (2015). (B) Zoom-in map of the red-square-marked area in map A, showing the palaeogeographic position (red stars) of the Bristol Channel Basin (with the Kilve section) and the Cleveland Basin (with the Ravenscar, Hawsker Bottoms and Staithes sections) at the northwestern end of the Tethys Ocean; (C) Modern map of the Bristol Channel with sample localities marked (modified after Ruhl *et al.*, 2010).

Fig. 2. Upper Triassic and Early Jurassic (Hettangian and early Sinemurian) $\delta^{13}C_{TOC}$ and TOC data from the Bristol Channel Basin sections at St. Audries Bay and East Quantox Head (Hesselbo et al., 2002, Ruhl et al., 2010; Hüsing *et al.*, 2014) showing a pronounced ~3 ‰

negative shift in $\delta^{13}C_{TOC}$ in the Lower Sinemurian *A. bucklandi* ammonite zone. Palaeomag data from Hounslow *et al.* (2004) and Hüsing *et al.* (2014). $\delta^{13}C_{TOC}$ and $\delta^{13}C_{CARB}$ data from the Bristol Channel Basin at Kilve (this study) show a similar ~2–3 ‰ negative excursion, coeval with the observations from East Quantox Head. The dark-grey coloured band represents the TOC-rich laminated black shale horizon as in Figure 2. The blue coloured band represents the stratigraphic level of methane-seep occurrence at the Lower Sinemurian fore-shore outcrops at Kilve.

Fig. 3. Sedimentary description and geochemical and palynological results from the *A. bucklandi* ammonite Biozone of Kilve, Somerset, UK. Geochemical data, including $\delta^{13}C_{TOC}$, $\delta^{13}C_{carb}$, TOC (measured by Coulomat) and HI are in black and grey squares. Palynological results including (% *Classopollis meyeriana*) / (total terrestrial palynomorphs), (% *Tasmanites* spp.) / (total microplankton), (% marine palynomorphs) / (total marine + terrestrial) and (% AOM) / (total kerogen) are in black circles (AOM = amorphous organic matter). Levels of methane seepage and organic-rich black shale occurrence are marked by, respectively, blue and grey bands. A pseudo-Van Krevelen diagram (with HI *vs* Tmax) is given on the left (following Delvaux *et al*., 1990), with red squares representing samples from the level of the negative carbon-isotope excursion (CIE).

Fig. 4. Outcrop and methane seep-mound images and associated geochemical data from Kilve (Somerset, UK) and Ravenscar (Yorkshire, UK). Photographs (A), (B), (C) and (D) show methane seep-mounds from Kilve. Photograph (E) shows a methane seep-mound from Ravenscar. The cross-plots between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$: Red circles represent values from the Lower Sinemurian methane seep-mounds at Kilve (Allison *et al*., 2008; Price *et al*., 2008) and the Early Toarcian methane seep-mounds at Ravenscar (this study). Light grey diamonds represent values from Lower Sinemurian mudrocks at Kilve, which formed stratigraphically before and after the methane seep-mounds (Allison *et al*., 2008). Pink triangles represent values from mudrock samples from the mound-bearing bed, in close proximity (1–20 m) to the seep-mounds (Price *et al*., 2008). Dark grey squares represent values for the Lower

Sinemurian mudrocks in the Kilve cliff-section, ~50 m away from the nearest visible seep-mound (this study). Dark grey squares also represent Lower Toarcian belemnite values from Yorkshire (McArthur *et al.*, 2000). Photograph (F) illustrates the sampled outcrop succession with black-shale interval and methane seep level marked in yellow and blue.

Fig. 5. Multi-taper (MTM; 3π) power spectra of the obtained $\delta^{13}C_{TOC}$ and TOC time series (after Ruhl *et al.* (2010) and Hüsing *et al.*, 2014) 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). A) $\delta^{13}C_{TOC}$ time-series multi-taper power spectrum of the complete data-set as in Figure 5, showing dominant short ~100 kyr eccentricity and long 2–2.4 myr astronomical forcing. B) Multi-taper power spectrum of the high frequency (0 – 0.8 Myr) band-pass filter of the $\delta^{13}C_{TOC}$ time-series, showing dominant short (~100 kyr) and long (~405 kyr) eccentricity. C) TOC time-series multi-taper power spectrum of the complete data-set as in Figure 5, showing dominant short (~100 kyr) eccentricity and long 405 to 2–2.4 myr astronomical forcing. $\delta^{13}C_{TOC}$ and TOC time-series data was first manipulated to give uniform sample spacing using linear interpolation. 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).

Fig. 6. Upper Triassic to Lower Jurassic (Uppermost Rhaetian to Lower Sinemurian) $\delta^{13}C_{TOC}$ and total organic carbon (TOC) composite from the Westbury, Lilstock and Blue Lias Formation at St Audries Bay, East Quantoxhead and Kilve (Somerset, UK) (this study; Hesselbo *et al.*, 2002; Ruhl *et al.*, 2010; Hüsing *et al.*, 2014), plotted against absolute time following bio-, magneto- and cyclostratigraphic and radiometric correlation between the Bristol Channel Basin (UK), the Newark and Hartford Basins (USA), the Fundy Basin (Canada), the Pucara Basin (Peru), New York Canyon (Nevada, USA) and the La2010[a/b/c/d] astronomical solutions (this study; Hesselbo *et al.*, 2002; Hounslow *et al.*, 2004; Kent and

Olsen, 2008; Ruhl *et al.*, 2010; Schoene *et al.,* 2010; Laskar *et al.*, 2011; Blackburn *et al.*, 2013; Hüsing *et al.*, 2014; Sell *et al.*, 2014).

Fig. 7. A suggested model explaining subsequent phases of change in the environmental and depositional environment leading to methane seep-mound formation, sourced by shallow subsurface biogenic methane production. Development of organic-rich, anoxic, black shales and the formation of biogenic methane by microbial methaneogenesis potentially led to overpressure in the pore-space and a flux of methane to the sediment-water interface. Subsequent compaction and/ or cementation of the overlying host-rock and significant closure of pore space forced free methane to be channelled up along fractures and faults, leading to highly localized methane fluxes into the overlying water-column and precipitation of calcareous mounds on the sea floor.

Fig. 8. Lithostratigraphy of the Lower Sinemurian in the Bristol Channel Basin at the Kilve section (Somerset, UK) and the Lower Toarcian in the Cleveland Basin at the Ravenscar section (Yorkshire, UK). The methane-seep horizons in both sections are marked by the blue coloured band and occur stratigraphically above the laminated organic-rich black shale intervals. The organic-rich laminated black shale intervals in both sections are marked by the grey band. TOC records are from this study (Kilve) and Kemp *et al.*, 2011 (Yorkshire).

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