Molecular and petrographical evidence for lacustrine environmental and biotic change in the Sichuan mega-lake (China) during the Toarcian Oceanic Anoxic Event

Weimu Xu [a,b,*], Johan W.H. Weijers [c], Micha Ruhl [a,d], Erdem F. Idiz [a], Hugh C. Jenkyns [a], James B. Riding [e], Olga Gorbanenko [a], Stephen P. Hesselbo [f]

[a] Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, UK
[b] School of Earth Sciences, University College Dublin, Belfield, Dublin 4, Ireland
[c] Shell Global Solutions International B.V., Shell Technology Centre Amsterdam, Grasweg 31, 1031 HW, Amsterdam, The Netherlands
[d] Department of Geology, Trinity College Dublin, College Green, Dublin 2, Ireland
[e] British Geological Survey, Keyworth, Nottingham NG12 5GG, UK
[f] Camborne School of Mines and Environment and Sustainability Institute, University of Exeter, Penryn Campus, Penryn, Cornwall TR10 9FE, UK
[*] Corresponding author: weimu.xu1@ucd.ie

ABSTRACT

The organic-rich upper Lower Jurassic Da'anzhai Member (Ziliujing Formation) of the Sichuan Basin, China, is the first stratigraphically well-constrained lacustrine succession associated with the Toarcian Oceanic Anoxic Event (T-OAE; ~183 Ma). The formation and/or expansion of the Sichuan mega-lake, likely one of the most extensive fresh-water systems to ever have existed on the planet, is marked by large-scale lacustrine organic productivity and carbon burial during the T-OAE, possibly due to intensified hydrological cycling and nutrient supply. New molecular biomarker and organic petrographical analyses, combined with bulk organic and inorganic geochemical and palynological data, are presented here, providing insight into aquatic productivity, land-plant biodiversity, and terrestrial ecosystem evolution in continental interiors during the T-OAE. We show that lacustrine algal growth during the T-OAE accounts for a significant organic-matter flux to the lakebed in the Sichuan mega-lake. Lacustrine water-column stratification during the T-OAE likely facilitated the formation of dysoxic-anoxic conditions at the lake bottom, favouring organic-matter preservation and carbon sequestration into organic-rich black shales in the Sichuan Basin at that time. We attribute the palaeo-Sichuan lake expansion to enhanced hydrological cycling under a high-seasonality climate in the hinterland during the T-OAE greenhouse.

Key words: Toarcian, Oceanic Anoxic Event, lacustrine environment, organic-rich black shale, Sichuan Basin, molecular biomarkers, organic petrography, palynology

1. Introduction

The early Toarcian Oceanic Anoxic Event (T-OAE; ~183 Ma), one of the most intense and geographically extensive events of oceanic redox change and accompanying organic-carbon burial in the Mesozoic Era, is well expressed in both marine and lacustrine environments from both hemispheres (e.g., Jenkyns, 1985, 1988, 2010; Al-Suwaidi et al., 2016; Xu et al., 2017). The T-OAE is marked by major changes in global geochemical cycles, with an apparently rapid negative shift of up to 8‰ in terrestrial and marine bulk sedimentary organic matter and a typically smaller (3–6‰) negative excursion in specific organic molecules and carbonate archives (Hesselbo et al., 2000, 2007; Sælen et al., 2000; Schouten et al., 2000; Jenkyns et al., 2002; Kemp et al., 2005; Hermoso et al., 2009; French et al., 2014; Suan et al., 2015; Xu et al., 2017, 2018*a*). This negative carbon-isotope shift, which is contained within an overall positive excursion, has been variously linked to volcanogenic carbon dioxide (CO_2) degassing during the emplacement of the Karoo-Ferrar large igneous province, the associated degassing from dyke- and sill-intruded subsurface organic-rich shales, and/or by seafloor methane (CH_4) clathrate dissociation (Duncan et al., 1997; Hesselbo, et al., 2000; Kemp et al., 2005; McElwain et al., 2005; Svensen et al., 2007; Percival et al., 2015, 2016; Xu et al., 2018*b*). The doubling–tripling of early Toarcian elevated atmospheric pCO_2 (McElwain et al., 2005; Li et al., 2020), likely resulted in intensified hydrological cycling and increased silicate weathering, thereby increasing delivery of riverine nutrients to the oceans and large lakes (Brazier et al., 2015; Dera et al., 2011; Jenkyns et al., 2002, 2003; Jenkyns, 2010; Xu et al., 2017, 2018*a*).

Marine depositional environments exhibited enhanced burial of organic matter, likely due to increased primary productivity and a subsequent carbon flux to the sea floor during the T-OAE (Jenkyns, 2010). The development of oceanic anoxia/euxinia extended over globally distributed basins and sub-basins of shallow shelves, commonly characterized by water-column stratification, across deeper water continental margins to the deep central palaoe-Pacific and led to increased sedimentary organic-matter preservation and carbon sequestration (Farrimond et al., 1989; Jenkyns, 2010; Gröcke et al., 2011; French et al., 2014; Ikeda et al., 2018; Xu et al., 2018*a*).

Elevated hydrological cycling linked to global warming and the expansion of shallow marine coastal environments as a result of contemporaneous early Toarcian eustatic sea-level rise, likely promoted the increased flux of humidity into continental interiors resulting in the formation and/or significant expansion of major lake systems in continental basins across the eastern Pangean landmass (Jenkyns, 2010; Xu et al., 2017; Huang et al., 2018; Jin et al., 2020; J. Liu et al., 2020; M. Liu et al., 2020). A mega-lake several times the size of Lake Superior, presently the geographically largest lake on Earth, developed into a much bigger area in the Sichuan Basin, China, coinciding with the T-OAE (Xu et al., 2017).

Lacustrine primary productivity and the development of anoxic conditions in the Sichuan mega-lake led to major carbon drawdown and sequestration into the organic-rich black shales of the Da'anzhai Member of the Ziliujing Formation that formed in the Sichuan Basin during the T-OAE (Xu et al., 2017; J. Liu et al., 2020). This lacustrine carbon burial, estimated to be ~460 Gt of organic carbon, likely significantly impacted the global exogenic carbon cycle, and led to a more rapid recovery of the global carbon-cycle perturbation associated with the T-OAE (Xu et al., 2017). The organic-rich black shales of the Da'anzhai Member are rich hydrocarbon source rocks in the areas of the basin that underwent thermal maturation conducive to oil and gas generation (Zhu et al., 2007; Zou, 2013; Wang et al., 2018).

Deposition of the lacustrine organic-rich black shales of the Da'anzhai Member was marked by major changes in the type and concentration of sedimentary organic matter (Xu et al., 2017; J. Liu et al., 2020; Wang et al., 2018), but little is known about its composition, thereby hampering the understanding of environmental processes and biotic changes in the early Toarcian Sichuan mega-lake and its hinterland. Here, we present the first extractable molecular (lipid) biomarker data, combined with carbon-isotope ratios of the non-extractable organic matter. Together with new organic petrographical results, and set in the context of previously published palynological, bulk and molecular compound-specific organic-carbon isotope, and Rock-Eval data, we (1) determine (changes in) the nature of the sedimentary organic matter within the Da'anzhai Member, and (2) improve understanding of changes in the environmental, depositional and ecosystem conditions in the Sichuan mega-lake and across its hinterland, during the T-OAE.

2. Geological setting and background

The present-day geographical Sichuan Basin covers an area of ~230,000 km^2 (Cai et al., 2003), three times the area of Lake Superior, with the Early Jurassic equivalent (and the palaeo-Sichuan mega-lake system) thought to have been even larger (Guo et al., 2011; Xu et al., 2017; Fig. 1). The Sichuan Basin formed on the western part of the Yangtze Platform and sedimentation commenced with the Neoproterozoic Sinian Sequence (850–570Ma; Ryder, 1991). Shallow-marine carbonates formed from the Late Paleozoic to the Middle Triassic, with occasional epeirogenic events, e.g. widespread basalt emplacement due to extension of the western margin of the Yangtze Platform in the Late Palaeozoic (Ryder, 1991). Sedimentation switched from marine to continental in the Middle to Late Triassic with Indosinian tectonic uplift due to closure of the Palaeotethys and collision of the North and South China cratonic blocks (Cai et al., 2003). Sandy to conglomeratic sediments were deposited as alluvial fans and lakeshore–deltaic plain facies in the Early Jurassic, particularly along the southern front of the Longmen and Micang-Daba mountain ranges at the north-western and northern margins of the Sichuan Basin (He and Zhu, 2012; Guo et al., 2011; Ryder, 1991; Zou, 2013; Fig. 1). Continental/ fluvial deposits and red palaeosol horizons, with pedogenic carbonate nodules, mark the Ma'anshan Member (middle Ziliujing Formation) and underlie the lacustrine facies of the upper Lower Jurassic (Toarcian) Da'anzhai Member (uppermost Ziliujing Formation). The Toarcian Da'anzhai Member represents the development of, or transition to, lacustrine conditions and the formation of a major lake (Fig. 2). Lacustrine conditions may, however, have persisted through most of the Early Jurassic in the most central and deepest part of the basin, although their onset and termination are still poorly dated (Li and He, 2014; J. Liu et al., 2020).

The lacustrine depositional setting for the Jurassic Da'anzhai Member was identified based on the occurrences of the bivalve genus *Margarififera* and the freshwater/brackish alga *Botryococcus*, together with molecular biomarker evidence from tetracyclic polyprenoids (Wang et al., 2010; Xu et al., 2017). Recent studies have indicated potential marine incursions into the palaeo-Sichuan mega-lake based on the sporadic occurrence of acritarchs, prasinophytes and other marine palynomorphs in parts of the Da’anzhai Member, likely associated with global marine transgression during the early Toarcian (Xu et al., 2017). Elevated basin-water salinities may also be indicated by increased major- and trace-elemental ratios (J. Liu et al., 2020). However, the depositional environment is thought to be dominantly lacustrine, with minor marine incursions only having occurred after the formation and expansion of the Sichuan mega-lake (Xu et al., 2017).

The two cores studied here are located in the more proximal-to-shore part of the palaeo-Sichuan lake (Fig. 1). Core A (~50 m) and Core B (~70 m) penetrated almost the complete Da’anzhai Member, including ~4 m of palaeosol sediments of the Ma’anshan Member at the base of the sampled interval (Fig. 2; Xu et al., 2017). The Lower Toarcian lacustrine Da’anzhai Member comprises fossiliferous limestone with freshwater bivalves and ostrocods, dark mudstone and laminated black shale (Xu et al., 2017). The lower half of the Da’anzhai Member in Core A is predominantly interbedded fossiliferous limestones and organic-poor mudstones. By contrast, the upper ~20 m is mainly organic-rich laminated black shale, interbedded with fossiliferous limestone at a metre-scale and representing the deepest phase of the palaeo-Sichuan mega-lake (Fig. 2; Xu et al., 2017). The top of Core A comprises two fossiliferous limestone beds, each ~3.5 m thick (Fig. 2; Xu et al., 2017). The more proximal Core B is richer in carbonate, and the fossiliferous limestones contain larger and more complete shell fragments than those in Core A, locally even in life-position. The shells in the fossiliferous limestones of Core B are also more homogenous in size and likely represent the same species. The organic-rich black shales in the lower half of Core B are generally unlaminated and often contain thin shell fragments (Fig. 2; Xu et al., 2017).

The established stratigraphical framework for the Da’anzhai Member in the Sichuan

Basin was based on micro- and macrofossil biostratigraphy, carbon-isotope chemostratigraphy and Re-Os geochronology. The palynomorph assemblages and abundance of the lacustrine Da'anzhai Member are comparable to floras from lower Toarcian marine successions in northern Europe and Australia. These include the superabundance of the pollen *Classopollis* sp. (and the absence of *Callialasporites* spp.), the occurrence of the spore *Ischyosporites variegatus*, the acritarch *Veryhachium collectum*, multi-specimen clumps of the prasinophyte *Halosphaeropsis liassica* and the rare occurrence of the dinoflagellate cyst ?*Skuadinium* sp., indicating that the successions studied here are of Early Toarcian age. Re-Os radioisotopic dating provides an isochron of 180±3.2 Ma. Combined with the negative carbon isotope excursion, similar in magnitude to Toarcian marine records, deposition of this lacustrine succession is suggested to have directly coincided with the T-OAE, corresponding to the late *tenuicostatum–falciferum* Zone of the north European ammonite province (Xu et al., 2017; J. Liu et al., 2020).

3. Materials and methods

3.1 Samples and analytical overview

TOC and Rock Eval data, carbon-isotope profiles of the bulk organic matter ($\delta^{13}C_{TOC}$) and the long-chain (leaf-wax) *n*-alkanes ($\delta^{13}C_{n\text{-alkanes}}$), major- and trace-element concentrations and palynomorph assemblages of the Da’anzhai Member in cores A and B, were previously reported in Xu et al. (2017). Based on these data, 22 samples from Core A and 5 samples from Core B were selected for detailed analyses of the extractable molecular biomarker fractions. Furthermore, 6 samples from high-TOC black shales in Core A, spanning the negative CIE reflecting the carbon-cycle perturbation associated with the T-OAE, were selected for organic petrography/maceral analyses. In addition to the previously published $\delta^{13}C_{TOC}$ and $\delta^{13}C_{n\text{-alkanes}}$ data, and Rock Eval analyses on bulk-rock materials, carbon-isotope and Rock Eval analyses were also undertaken on the residual organic matter, after solvent extraction (22 samples from Core A and 5 samples from Core B), to further constrain global carbon-cycle change at this time by eliminating any possible effect of contamination by migrated hydrocarbons on the carbon-isotope signature of sedimentary organic matter.

3.2 Biomarker analysis

Sample preparation and molecular biomarker analysis was undertaken at the Organic Geochemistry Laboratory facilities at Shell Global Solutions International in Rijswijk, Netherlands. Total lipid extracts (TLE) were obtained by extraction using a Dionex ASE® 350 Accelerated Solvent Extractor (ASE), as described in Xu et al. (2017).

The TLE were analyzed using an Agilent 7890A Gas Chromatograph (GC)-Flame Ionization Detector (FID) to examine the overall distribution of normal, branched and cyclic alkanes and aromatic compounds. An Agilent Ultra 1 column (50 m × 0.2 mm internal diameter, 0.11 μm film thickness) was used with the following temperature program for the oven: 35°C (5 min) – 4°C/min – 325°C (15 min). Samples were injected splitless and the injector was set at 325°C. Helium was used as carrier gas with a flow rate of 25 cm/sec (0.47 ml/min).

An aliquot of the TLE was separated over $AgNO_3$-impregnated silica-gel columns into saturate, aromatic and resin fractions. After pre-conditioning of the column with cyclohexane and application of the TLE, the saturate fraction was eluted with *n*-hexane, the aromatic fraction with toluene and the resin fraction with acetone (3 column volumes each). A mixture of known amounts of standard compounds was added to the aromatic fraction at this stage prior to analysis using Gas Chromatography/Mass Selective Detection. The retrieved saturate fraction of each sample was subsequently separated into n-alkane and branched/cyclic alkane fractions (Xu et al., 2017).

Branched/cyclic (b/c) fractions were analyzed using an Agilent 7890A GC system coupled to an Agilent 7000 Triple Quadrupole Mass Spectrometer. Samples were injected splitless. Separation of compounds was achieved on a J&W DB-1 phase column (60 m × 250 μm, 0.25 μm film thickness) using the following temperature program: 50°C (1 min) - 4°C/min - 220°C – 1.2 °C/min – 280°C – 3°C/m – 310°C (20 min.). The temperature of the ion source was set at 250°C and the collision energy in the second quadrupole was set at 10. A selected set of parent–daughter mass transitions was scanned to monitor the compounds of interest. Compounds were identified in the respective mass transition chromatograms by comparison of their retention times and elution order to standard samples. For selected samples the system was run in full scan GC/MS mode to confirm identifications with full mass spectra.

Aromatic fractions were analyzed using an Agilent 7890B GC system coupled to an Agilent 5973 Mass Selective Detector (MSD). Samples were injected splitless. Separation of compounds was achieved on a J&W DB-1 phase column (60 m × 250 μm, 0.25 μm film thickness) using the following temperature program: 50°C (1 min) - 20°C/min - 120°C - 2°C/min – 320°C (20 min.). The source temperature of the MSD was set at 250°C and it was run in selective ion mode (SIM) scanning for the masses of interest. Compounds were identified in the respective mass chromatograms by comparison of their retention time and elution order with standard samples.

3.3 Carbon-isotope analysis of non-solvent-extractable sedimentary organic matter (sample-residue after ASE-extraction)

Bulk $\delta^{13}C$ analyses were performed on decarbonated and homogenized residual organic matter in the sample after ASE solvent-extraction (Xu et al., 2017). 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, at the Research Laboratory for Archaeology and History of Art (RLAHA), University of Oxford, UK. 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. The in-house RLAHA alanine standard is checked weekly 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‰.

3.4 Rock-Eval pyrolysis on non-solvent-extractable sedimentary organic matter (sample-residue after ASE-extraction)

Rock-Eval analyses were performed on homogenized residual organic matter in the sample after ASE solvent-extraction (Xu et al., 2017), with a Rock-Eval 6 Standard Analyzer unit from Vinci Technologies, at the Department of Earth Sciences, University of Oxford. These analyses provided direct and derived data for S1, S2, TMax, $S3_{co}$/ $S3_{co_2}$ (New Oxygen Index), $S4_{co}$/ $S4_{co_2}$ (Residual Organic Carbon) and S5 (Mineral Carbon), to calculate the Total Organic Carbon (TOC, in wt. %), Hydrogen Index (HI, in mg HC/ g TOC) and Oxygen Index (OI, in mg CO_2/g TOC). Details of these parameters are explained in Behar et al. (2001). Laboratory procedures were essentially similar to Behar et al. (2001) and as described in Xu et al. (2017). TOC data measured by Rock-Eval 6 are more reliable than those obtained by Leco, because of the need of a decarbonation step prior to Leco measurement, during which a part of the organic carbon may be hydrolysed and lost (Behar et al., 2001).

3.5 Organic Petrology

A total of 6 samples (3 cm in diameter) from Core A were cut perpendicular to the bedding plane, embedded in epoxy resin, and subjected to dry polishing to avoid swelling of clay minerals (Gorbanenko, 2017). Semi-quantitative and qualitative analyses were carried out using a Leica DMRX microscope at the Department of Earth Sciences, University of Oxford. The polished blocks were analyzed in both reflected white light and fluorescence illumination, under oil immersion and at a magnification of ×500. Vitrinite reflectance was estimated based on the rare occurrence of detrital vitrinite in the samples. The nomenclature of Taylor et al. (1998) was used for the description of macerals of the vitrinite and inertinite groups, and that of Hutton (1987) for the liptinite group.

4. Results

4.1 Rock-Eval and carbon-isotope record of sample residues after ASE-extraction

Rock-Eval pyrolysis, performed on the residual sample powder, after ASE-extraction, shows TOC values of ~0.3 to ~2.5 wt. %, hydrogen index (HI) values of ~60 to ~320 mg HC/ gTOC, and production index (PI) values of ~0 to ~0.095 (Fig. 3). As expected, these values are lower compared to values obtained from whole-rock Rock-Eval analyses of the same samples, with TOC values of 0.7–3.0 wt. %, HI values of 98–393 mg HC/g TOC and PI values of 0.15–0.34 (Xu et al., 2017).

Carbon-isotope analysis of the residual, non-solvent-extractable organic matter (after ASE-extraction), shows values of -29.0 to -22.7 ‰ for Core A, and -26.4 to -23.5 ‰ for Core B (Fig. 3). The obtained organic carbon-isotope records from the residual organic carbon follow similar trends compared to the bulk sedimentary organic matter. Values from the residue in the organic-rich upper half of the Da'anzhai Member in Core A (from ~2700m upward), are however 0–1‰ more positive compared to bulk-rock $\delta^{13}C_{TOC}$ values (Fig. 3).

4.2 Organic petrology

Six samples from Core A, with TOC values of 0.69 wt. % to 2.25 wt. %, HI values of 194 to 386 mg HC/g TOC, and T_{max} values of ~449–453°C, were analyzed for organic petrography. All 6 samples were qualitatively and semi-quantitatively characterized for the constituent major maceral groups present, including vitrinite, inertinite and liptinite (Fig. 5; Table 1; Supplementary Fig. 1).Vitrinite group macerals are rare, being dominated by oxidized or reworked allochthonous particles, and a minor amount of autochthonous components. Inertinite group macerals are more abundant and are dominated by fusinite, with some semifusinite, inertodetrinite and secondary micrinite. Funginite particles, likely resulting from fungal and microbial degradation, are observed in several samples (Fig. 5-E). Measurement of the rare occurrence of autochthonous vitrinite gives a vitrinite reflectance (VR) of ~0.82–0.85%R_0 (personal communication with George Siavalas at Shell International).

Liptinite, the generally more H-rich and fluorescing maceral group, is subdivided into primary and secondary types. The observed primary liptinite types include sporinite, alginite and liptodetrinite, whereas the secondary liptinite types include migrabitumen and oil droplets. Sporinite, exhibiting an orange fluorescing colour, is observed in several samples but not quantified (Fig. 5-C). The alginite group is further subdivided into telalginite and lamalginite, derived from thick-walled unicellular algae and thin-walled unicellular planktonic or benthic algae, respectively (Hutton, 1987). The telalginite and lamalginite show yellow to orange fluorescing colours of moderate intensity (with lamalginite showing a slightly lower intensity), indicating oil-window maturity. Significantly, a high proportion of telalginites in Core A comprises the green alga *Botryococcus* as well as other freshwater algae (*Pediastrum*?) and several acritarchs and prasinophytes (Fig. 5-A, B), in agreement with the previous palynological study on the same core (Xu et al., 2017). Rare filamentous lamalginite, exhibiting moderate fluorescence (lower than that of telalginite), was observed in a sample from depth 2702.13 m in Core A.

Apart from the recognizable primary macerals, there are also varying amounts of bituminite (amorphous organic matter; AOM) dispersed in the groundmass, which is commonly very fluorescent and indicative of H-rich substrates. Oil droplets are observed mainly in the pore space of zooclasts. *Botryococcus*-derived telalginites are commonly observed close to the oil droplets, with some transitioning into a bitumen phase, indicative of incipient conversion to oil (Fig. 5-A).

4.3. Extractable Organic Matter

The molecular biomarker compositions of the 22 samples in Core A were studied by analyses of the extractable lipid fractions comprising straight-chain *n*-alkanes and acyclic isoprenoids, branched/cyclic (penta-, tetra- and tricyclic) terpanes, and aromatic lipids.

4.3.1 Total Lipid Extracts (TLE)

The GC-amenable fractions of the TLE from selected samples from core A show a clear dominance of *n*-alkanes, with subordinate amounts of branched, cyclic and aromatic fractions, indicating a highly paraffinic composition (Fig. 6).

The *n*-alkane profile exhibits a clear depth-trend in the relative proportions of the short-, intermediate- and long-chain lengths in Core A (Fig. 6). Samples from the carbonate-rich lower Da'anzhai Member (at 2705.135 m and 2710.73 m in the lower half of the core; marked by low TOC and low HI values) exhibit a dominance of short-chain (e.g. C_{13} or C_{15})

n-alkanes (Fig. 6). The concentration of the mid-chain length (e.g. C_{23} or C_{25}) *n*-alkanes increases in the TLE of samples from the lower part of the black-shale interval, stratigraphically in the middle of the Da'anzhai Member (at 2691.25 m and 2695.57 m in the middle of the core; marked by increasing TOC and HI values; Fig. 6). Samples from the main interval of black-shale formation in the upper part of the Da'anzhai Member (at 2677.5 m and 2681.17 m, in the upper part of the core; marked by highest TOC and HI values) exhibit high concentrations of mid-chain length (e.g. C_{23} or C_{25}) *n*-alkanes, typically showing a bimodal chain-length distribution pattern (Fig. 6). The pristane (Pr) and phytane (Ph) isoprenoid abundance is much lower relative to the *n*-alkanes in all studied samples, with Pr/*n*-C_{17} ratios of 0.04–0.26 and Ph/*n*-C_{18} ratios of 0.08–0.25. The Pr/Ph ratios are between 0.82 and 1.57.

4.3.2 Pentacyclic triterpenoids

The hopane occurrence and distributions in the Da'anzhai Member of both cores shows unique features with strikingly high concentrations of rearranged hopanes, including 17α(*H*)-diahopanes, 18α(*H*)-neohopanes and the 'early eluting' hopanes (9,15 dimethyl-25,27-bisnorhopanes; Nytoft et al., 2007) (Fig. 7). The 17α, 21β hopane, diahopane and early eluting hopane with carbon numbers C_{31} to C_{35} all exhibit the S and R isomer doublets and their concentrations generally decrease as the carbon number increases. Another rearranged hopane, C_{29} 28-*Nor*-spergulane (29Nsp; mass transition 398→191; Fig. 7), is also present (Nytoft et al., 2006) (Fig. 7).

Gammacerane was identified and quantified by GC/MSxMS parent–daughter mass transition *m/z* 412→191, the same transition where the 17α-hopane (C_{30} hopane) also appeared. The gammacerane concentration, reported relative to the C_{30} hopane and commonly used as an index indicative of the degree of water-column stratification

(Sinninghe Damsté et al., 1995), ranges between 0.05 and 0.23, with the highest value occurring at depth 2681.17m in Core A (Fig. 10).

Observed 3β-methylhopanes, likely (mainly) derived from methane-oxidising bacteria and commonly abundant in lake settings, were identified in the GC/MSxMS precursor–product mass transition *m/z* 426→205 (Farrimond et al., 2004; Brocks et al., 2005; Welander and Summons, 2012), albeit in low concentrations. 3β-methylhopane index values range between 2.87% and 6.77% (the percentage for 3β-methylhopanes relative to C30 Hopane; Kiepper et al., 2014).

4.3.3 Tetracyclic triterpenoids

The precursor–product mass transition *m/z* 414→217 does not show obvious peaks in any of the samples analyzed, indicating the near absence of C_{30} steranes (24-*n*-propylcholestanes), normally sourced from marine algae (Fig. 8). Dinosteranes, sourced from dinoflagellates, were also not found in any of the samples studied (mass transition *m/z* 414→98), despite the sporadic presence of dinoflagellate cysts in palynological residues (Xu et al., 2017).

The distributions of C_{27}, C_{28} and C_{29} steranes, exemplified by the *m/z* 217 mass-chromatogram (GC/MS) traces aligned with the precursor–product mass transitions (Fig. 8), show only a limited variation between different samples. However, all samples show high concentrations of diasteranes relative to steranes (Figs 8, 9). Sterane/hopane ratios, calculated as regular steranes/17α-hopanes (Moldowan et al., 1985), range from 0.45 to 1.50 (Fig. 10).

Observed C_{30} tetracyclic polyprenoids (TPP) were analysed and detected by GC/MSxMS, with parent–daughter mass transition *m/z* 414→259, showing the two peaks of TPPa and TPPb (C_{30} TPP 18α(H), 21R and C30 TPP 18α(H), 21S doublet) (Holba et al., 2000; Xu et al., 2017). The TPP ratios, peak areas of a C_{30} tetracyclic polyprenoid divided by the sum of the peak areas of the C_{26} 27-norcholestanes (TPP ratio = (2 x peak a)/[(2 x peak a) + (Σ 27-norcholestanes)]; Holba et al. 2000), are calculated here for all the samples studied (Fig. 10). The values of TPP ratios ranges between 0 and 0.44.

4.3.4 Tricyclic terpanes

Tricyclic and pentacyclic terpanes, observed in the *m/z* 191 mass chromatogram and with C_{19} to C_{31} chain-lengths, were detected in all samples. C_{29} to C_{31} tricyclic terpanes are, however, only present in small amounts and are not obvious in the GC/MS mass chromatogram (Supplementary Fig. 4). The C_{25} to C_{31} tricyclic terpanes all have S and R isomers. All samples are marked by exceptionally high C_{21} tricyclic terpane concentrations (Supplementary Fig. 4).

The studied samples are marked by the noticeable absence of terpane biomarkers for terrestrial higher plants. Peaks of pimarane, rimuane, isopimarane were not found in the GC/MSxMS mass transition *m/z* 276→247, although their nor-versions are present in the mass transition *m/z* 262→233.

4.3.5. Aromatic fractions

Studied samples generally show a low abundance of (or a low signal for) aromatic compounds, including low abundances of dibenzothiophene (DBT: *m/z* 184) and phenanthrene (*m/z* 178) (Hughes et al., 1995). Isorenieratane, a pigment of photosynthetic green sulphur bacteria *Chlorobiaceae*, is not found in any of the samples studied. Terpane biomarkers, whose presence is generally indicative for the supply of terrestrial higher plant organic matter, are absent in all the samples studied. Perylene (*m/z* 252) was identified in all the samples studied. Perylene is an early diagenetic product derived from its nature precursors, which has been suggested to be kinds of black pigments sourced from terrestrial plants, fungi, insects, as well as aquatic diatoms and crinoids (Aizenshtat, 1973, Jiang et al., 2000 and references therein). Given the age of the sediments and the lacustrine depositional environment, terrestrial sources of plants, fungi and insects are the likely sources for the perylene in the Da'anzhai Member.

5. Discussion

5.1. Thermal maturation of organic matter in the Da'anzhai Member

The thermal maturity of Core A is estimated to be at peak oil window based on a series of parameters. Tmax ranges between 444 and 460°C (Fig. 10) and such values are in alignment with the observed vitrinite reflectance (VR) values of around 0.8–0.9%Ro. Production indices (PI; ratio of S1/(S1+S2)) range from 0.15–0.34, indicating that labile kerogen has undergone cracking and has generated hydrocarbons, indicative of at least early oil window maturity. VR measured on a few reliable vitrinite particles is ~0.8–0.9%. The organic maceral alginite has dark yellow to orange fluorescing colours under UV light and the palynomorphs are mid-brown in colour under transmitted white light as revealed during palynological study (Xu et al., 2017), both indicating that the succession examined has undergone some thermal alteration, consistent with oil-window maturity.

All the samples have CPI values of ~1.0, showing little or no preference of either odd- or even-numbered alkanes, which is probably attributable to the maturity of the samples (Xu et al., 2017). Some samples do show vestiges of an odd-over-even predominance around C_{23}–C_{29} (e.g. samples 105 and 261), indicating an initially odd-over-even predominance with subsequent levelling out due to molecular cracking upon increased maturity (Fig. 6).

Core B is thermally more mature than Core A with higher Tmax values, mainly ranging from 453–470°C (excluding some abnormal values). Palynomorphs are consistently dark brown in colour under transmitted white light, an indicator of having achieved a higher maturation compared to Core A (Xu et al., 2017). This conclusion is consistent with the observation that Core B extracts contain significantly lower concentrations of biomarkers than Core A. As a result, no quantifications of biomarker concentrations or ratios have been possible on Core B.

5.2. Clay-catalysed diagenesis of molecular biomarkers in the Da'anzhai Member

The hopanes in the Da'anzhai Member of Core A show atypical distributions with strikingly high concentrations of rearranged hopanes, including 17α(*H*)-diahopanes, 18α(*H*)-neohopanes (Ts and 29Ts) and the early eluting hopanes (9,15 dimethyl-25,27-bisnorhopanes) (Fig. 7). This phenomenon has been reported previously for the Da'anzhai Member in Zhu et al. (2007) on oils from different wells and in Huang et al. (2020) on TLE from shales, which was interpreted as related to the high maturity and the enriched clay content of this source rock, deposited under oxic to suboxic and slightly acidic conditions. Diahopanes (15Me-27-nor hopanes) are most likely derived from the same precursor molecules as the normal hopanes but have undergone oxidation in the D-ring and rearrangement by clay-mediated acidic catalysis (Peters et al., 2005). This possibly explains why their occurrence is more enhanced in the black shale interval of Core A, where clay mineral content is more enriched (Fig. 9).

In the Da'anzhai Member sample set, another rearranged hopane, C_{29} 28-*Nor*-spergulanes (29Nsp), is also present and has previously been reported in oils generated from lacustrine source rocks in South East Asia (Nytoft et al., 2006), which might indicate a lacustrine source signature. Nonetheless, the 29Nsp was postulated to have formed by oxidation and rearrangement of precursor hopanes in a similar way to diahopane (Nytoft et al., 2006).

5.3. Biomass change in the Toarcian palaeo-Sichuan mega-lake

The carbon-isotope records generated from the sample residues after ASE-extraction from both Core A and Core B (Fig. 4) should represent the stratigraphical evolution in the carbon-isotope composition of the non-extractable sedimentary organic matter. The observed trend in the carbon-isotope ratios of the residues (after ASE-extraction) closely resembles the trend observed in the original total bulk organic matter, albeit with slightly more positive values in Core A. This feature, whereby the non-extractable residual organic matter is on average isotopically heavier (Fig. 4) than the corresponding extractable organic matter of the same sample, is commonly observed in sediments from most marine and lacustrine depositional environments. The fact that the trends of the organic carbon-isotope record from the total bulk-rock, the non-extractable residue and the long-chain *n*-alkanes are all similar, albeit slightly offset, suggests that the extractable organic matter is indeed likely derived from *in situ* organic matter and not from migrated hydrocarbons.

Organic matter of the Da'anzhai Member in Core A is mainly composed of type I/II kerogen for the black shale interval (where HI values are mostly above 300 mg HC/g TOC) and type II/III kerogen for the rest of the core (Fig. 3; following Delvaux *et al.*, 1990; HI and OI data from Xu et al., 2017)), in agreement with the highly paraffinic *n*-alkane distribution, the high abundance of AOM and the presence of *Botryococcus*. Given the maturity of the organic matter in Core A, the original HI and TOC were likely even higher than their current values. Changes in the organic matter from kerogen Type II/III in the interval of the pre-T-OAE negative CIE, to predominantly Type I/II in the interval within the CIE, suggests stratigraphical changes in the composition of the sedimentary organic matter towards a more hydrogen-rich, algae-derived component during the T-OAE interval (Fig. 3).

The TLEs are very paraffinic (with a dominance of *n*-alkanes over branched and other compounds), especially within the black-shale interval where the waxy *n*-alkane hump extends to higher C numbers, which is typical of lacustrine source rocks or oils, potentially related to low proportions of resinite relative to other macerals (Carroll and Bohacs, 2001). Long-chain *n*-alkanes (C_{27}, C_{29}, C_{31}), normally diagenetic products of higher plant leaf waxes or specific freshwater algae (e.g. *Botryococcus*), are present in all the samples (Eglinton and Hamilton, 1967; Derenne et al., 1988; Metzger et al., 1991). The lack of the odd-over-even predominance has been attributed to the maturity of the samples (Xu et al., 2017). However, the major constituent of the longer-chain *n*-alkanes in many of the samples is not the C_{27}, C_{29}, C_{31} *n*-alkanes, but rather the C_{21}, C_{23}, C_{25} *n*-alkanes. Such mid-chain *n*-alkanes (C_{21}, C_{23}, C_{25}), found in lacustrine source rocks, are thought to be sourced from aquatic macrophytes (submerged and floating plants) (Ficken et al., 2000), and/or break down from higher carbon numbers. The relative concentration of mid-chain *n*-alkanes (C_{21}, C_{23}, C_{25}) increases from very low values in the carbonate-rich lower half of Core A, to values similarly high to the short-chain *n*-alkanes in the TOC-rich laminated black-shale interval of the same core. This pattern suggests elevated input and preservation of aquatic macrophytes in the TOC-rich, upper part of Core A, and/or increased higher plant leaf wax or specific freshwater algae (cf. Cranwell, 1977).

A large amount of inertinite (fusinite, semifusinite, funginite) and a small amount of recycled and indigenous vitrinite is observed by means of organic petrography, with more frequent and larger particles in the lower part of the core (Fig. 5-E, F, G). By contrast, the percentage of AOM, ranging between 1% and 82% of the total kerogen observed during palynological study, increases in the black-shale interval with a peak at 2681.17 m (Fig. 11).

AOM or bituminite is the amorphous/structureless organic component whose origin is varied and difficult to characterize under the microscope. It could be sourced from degraded phytoplankton or bacterially derived sources, or higher plant components, or it could represent the diagenetic product of macrophyte tissue (Tyson, 1995). However, the fact that the AOM is fluorescent indicates a dominantly algal origin. Tetracyclic polyprenoid compounds (TPP), which have been suggested to be typically sourced from freshwater algae, are normally more abundant in oils and associated source rocks deposited under freshwater or brackish-water environments (Holba et al., 2000). The covariance of the AOM percentages and the TPP ratios further supports the suggestion that the AOM is dominantly algae-derived (Fig. 10). The sterane/hopane ratios are 0.45–1.50 and have higher values in the lower part of the core than in the upper part, where the ratios stay relatively constant (Fig. 10). Sterane/hopane ratios reflect the ratios between eukaryote and bacterial biomass, with higher values indicating relatively higher algal input (Peters and Moldowan, 1993). The absolute amount of algal input might have increased during deposition of the black-shale interval based on the TPP ratios, but accompanying bacterial activity should also have increased, resulting in a higher relative abundance of bacterially derived components, hence low Sterane/hopane ratios. The elevated input of algae is further supported by the increased percentage of C_{27} steranes, whose primary precursor is predominantly red algae (Huang and Meinschein, 1979), relative to the combined C_{27}, C_{28} and C_{29} sterane abundance (Fig. 11).

Relatively high bacterial activity in the Da’anzhai Member has been demonstrated by the high abundance of hopanes relative to steranes, particularly in the black-shale interval. The presence of 3β-methylhopane, mainly derived from methane-oxidising bacteria and commonly abundant in some lacustrine settings (Farrimond et al., 2004; Brocks et al., 2005; Welander and Summons, 2012), also hints at bacterially promoted methane oxidation when the Da’anzhai Member was deposited. In addition, the presence of funginite, an inertinite maceral derived from spores or remains of fungi, is another indication of bacterial oxidation (Fig. 5-E; Jeffrey and Chrysler, 1906).

5.4. Changing depositional conditions in the Toarcian palaeo-Sichuan mega-lake

The base of the Da’anzhai Member, which overlies the terrestrial Ma’anshan Member, is marked by the presence of characteristic lacustrine facies stratigraphically overlying palaeosols. The switch to lacustrine deposits indicates a rise in lake level (Xu et al., 2017; J. Liu et al., 2020). The lower half of the Da’anzhai Member in Core A is characterized by dominant fossiliferous limestones with bivalve and ostracod fragments, alternating with mudstones (Xu et al., 2017). This interval also has generally low TOC (~1 wt. %) and low HI values (~150 mg C/g TOC), and was possibly deposited in a near-shore environment with low aquatic organic-matter productivity and/or preservation. In addition, there are larger amounts of inertinite macerals, of also relatively larger particle size, observed in the lower part of Core A, another indication of a near-shore depositional environment. The transition from fossiliferous limestone to laminated black shale at ~2693 m suggests deepening of the lake environment. The transition from the shallower, turbulent-water facies of the lower Da’anzhai Member to the deeper, mostly low-energy facies of the upper Da’anzhai Member reflects the more proximal location of the depositional environment recorded in Core A. The more distal well LQ104X in the central, deeper part of the basin exhibits predominantly quiet-water lacustrine mudstones throughout the lower to central part of the Da’anzhai Member (from ~3583 to ~3520m in the core), stratigraphically preceding the negative CIE associated with the T-OAE (J. Liu et al., 2020). This stratigraphic pattern suggests that lacustrine conditions developed in the central parts of the basin preceding the T-OAE, and further confirms a basinal water-level rise leading up to the negative CIE, with flooding of more proximal environments, and subsequent deepening of the lake (*this study*; Xu et al., 2017; J. Liu et al., 2020). The large-scale expansion and deepening of the palaeo-lake system in the Sichuan Basin during the T-OAE is further suggested by the presence of filamentous algae (lamalginite), a shallow-water dweller (Valiela et al., 1997; Scheffer et al., 1997), in the sample at 2702.13 m, compared with the more abundant *Botryococcus* in the black-shale interval.

In response to a warming climate, rising lake level and elevated nutrient supply, algal productivity in near-surface environments likely increased, and physical and/or chemical stratification probably developed in the water column of the palaeo-Sichuan Lake. Lake stratification could be caused by the formation of thermo layers during warm weather, which would be more pronounced during the T-OAE. It might also be facilitated by differences in salinity, with first sea water incursion during certain times enhancing the lake water salinity, followed by freshwater brought into the surface by enhanced hydrological cycling. High algal productivity and water-column stratification subsequently promoted the low-oxygen bottom-water conditions and the formation of black shales, even in relatively proximal depositional settings. The geochemical indicators of such stratification and reduced oxygen levels are seen in elevated levels of the gammacerane index, which has been observed in coeval marine basins (Farrimond et al., 1989; French et al., 2014), and increased sedimentary molybdenum concentrations (with Mo > 20ppm) (Xu et al., 2017; J. Liu et al., 2020).

Tiny pyrite framboids (<5µm), observed under the scanning electron microscopy (SEM) and in the organic petrographical study, are present in the black-shale interval, whereas larger pyrite framboids or single crystals are observed in the carbonate-rich intervals. This suggests a transition from oxic conditions for the accumulation of the fossiliferous limestone to euxinic water-column conditions during black shale deposition (cf., Wilkin et al., 1996). However, the absence in all the samples studied of isorenieratane, a pigment of photosynthetic green sulphur bacteria *Chlorobiaceae* that thrive in water columns bearing free H_2S, suggests that euxinia did not rise into the photic zone (Koopmans et al., 1996). Alternatively, the apparent absence of isorenieratane is mainly due to the relatively high thermal maturity of the sediments rather than any environmental implications. The Pr/Ph ratio throughout Core A ranges between 0.8 and 1.6 (Fig. 11), possibly suggesting that anoxic to suboxic conditions occurred during deposition of the Da'anzhai Member (Didyk et al., 1978; ten Haven et al., 1987).

The DBT/phenanthrene ratios, which reflect the amount of sulphur in sedimentary organic matter (Hughes et al., 1995), are extremely low in all the samples studied, supporting the freshwater nature of the lake. However, they are consistently slightly higher in the lower half of the core, where TOC is low. By contrast, well LQ104X in the deeper, more central part of the basin exhibits elevated S/TOC values coinciding with the T-OAE in the Upper Da'anzhai Member and low S/TOC values preceding the negative CIE in the Lower Da'anzhai Member (J. Liu et al., 2020). One explanation may be that increased hydrological cycling during the T-OAE, which expanded and deepened the lake, also diluted the sulphate concentration, limiting its incorporation into organic matter, primarily in the more proximal environments of the existing waterbody, suggesting not only a stratigraphical but also spatial variability in water-column chemistry and depositional conditions in the Toarcian Sichuan Basin mega-lake. Alternatively, the low DBT/phenanthrene ratios in the black-shale interval could also be related to elevated sulphate reduction in a more reducing environment, with sulphur increasingly being removed from the system through pyrite burial, limiting availability for uptake by the organic matter. Combined, these two mechanisms may explain the relatively elevated bulk-rock sulphur concentrations in the black-shale interval; it likely reflects the increasing amount of pyrite burial, with the organically bound sulphur, indicated by DBT/phenanthrene ratios, being limited.

The top of Core A (from ~2673 to ~2665m) and the upper part of Core B (from ~3120 to ~3108m) comprise two thick (~4–6 m each) fossiliferous limestone intervals, interrupted by a thin shale layer, together indicating a drop in lake level around the end of the T-OAE. This significant, and possibly rapid shallowing of the lacustrine depositional environment is corroborated by the occurrence of shallow-lake mudstones, shelly beach facies and sand shoals even in the deeper, more central part of the basin as recorded in well LQ104X (J. Liu et al., 2020).

5.5. Palaeo-ecosystem on land and implications for regional climate

The T-OAE, and associated changes in climate and environments, has been studied in geographically widespread localities across both hemispheres. Most studies have, however, focused on marine successions and limited understanding exists on climatic and environmental change in continental interiors and their potential impact on terrestrial ecosystems (e.g. Pienkowski and Waksmundzka, 2009; Slater et al., 2019). Constraints on biomass composition and abundance, and the changes therein, in the lacustrine Sichuan Basin, provides geographically important insights into possible ecosystem change in the Eastern Euarasia landmass on the South China block, during a time of major Early Jurassic climatic upheaval.

Palynofloras in the hinterland of the early Toarcian Sichuan Basin are of low diversity (Xu et al., 2017), predominantly consisting of the gymnosperm pollen *Classopollis* spp., and undifferentiated bisaccate pollen, *Cerebropollenites macroverrucosus, Chasmatosporites* spp., *Perinopollenites elatoides* and *Vitreisporites pallidus*. *Classopollis* spp. make up between 73.7% and 99.7% of the overall palynomorph assemblages (Fig. 11). Most specimens consist of dispersed grains, but some tetrads (groups of four grains) are also present. *Chasmatosporites* can commonly be somewhat problematic to identify at a species level, but the majority of specimens in the studied samples appear to be *Chasmatosporites apertus* or *Chasmatosporites hians* (Xu et al., 2017). Pteridophyte spores are also present in relatively low numbers, and include frequent *Cyathidites* spp. and *Ischyosporites variegatus*. Other spores recorded include *Cibotiumspora juriensis*, *Contignisporites* sp., *Neoraistrickia* sp., *Osmundacidites wellmanii,* indeterminate forms and ?*Kraeuselisporites* sp. (Xu et al., 2017).

The dominance of *Classopollis* in the palynomorph assemblages is commonly observed also in other lower Toarcian successions (e.g. Slater et al., 2019; Houben et al., 2020). This genus is interpreted as being thermophilic and is a reliable proxy for hot/warm climatic conditions (Pocock and Jansonius, 1961; Srivastava, 1976; Vakhrameyev, 1981; Volkheimer et al., 2008). The parent plants were representatives of the drought-resistant, thermophilic and xerophytic Cheirolepidiaceae (Vakhrameyev, 1970; Francis, 1983), and have been interpreted as having thrived in coastal and upland slope habitats (Filatoff, 1975; Batten, 1975).

Bisaccate pollen, commonly attributed to a large spectrum of plants such as conifers (e.g. *Pinuspollenites* spp.) and seed ferns (e.g. *Alisporites* spp.) (Shevchuk et al., 2018), are dispersed widely by wind due to their air sacs. The abundance of bisaccate pollen grains suggests dry and cool climatic conditions associated with coniferous source areas (Pienkowski and Waksmundzka, 2009). The abundance of bisaccate pollen mirrors that of *Classopollis* spp., suggesting a warm/dry Early Toarcian climate in the palaeo-Sichuan Basin hinterland (Fig. 11).

Cerebropollenites macroverrucosus occurs in low abundances and was probably produced by an extinct relative of the extant conifer hemlock (*Tsuga*) or a Japanese umbrella-pine (*Sciadopitys*) (Fig. 11; Batten and Dutta, 1997; Dejax et al., 2007). *Cerebropollenites* has been recorded in high abundances from the Early Jurassic Toarcian of Greenland and Yorkshire (Koppelhus and Dam, 2003; Slater et al., 2019; Houben et al., 2020), suggesting a geographically widespread occurrence. The parent plants of

Perinopollenites elatoides are indicators of wet environments (Stukins et al., 2013); this species only occurs at two stratigraphic levels at the onset of the T-OAE negative CIE in the Da'anzhai Member of the Sichuan Basin (Fig. 11).

Chasmatosporites is probably attributable to the order Cycadales (Pocock and Jansonius, 1969), whose modern representatives are arid-adapted and thrive in subtropical and tropical regions (Vakhrameev, 1991). Although *Chasmatosporites* occurs only sporadically throughout the studied succession, and in low abundance, its occurrence is more common in the upper part of the Da'anzhai Member, coincident with the level of the T-OAE negative CIE, where *Classopollis* spp. also occurs in high abundance (Fig. 11). The spore *Ischyosporites variegatus* belongs to the largely tropical Family Schizaeaceae (Couper, 1958). Hence, the occurrence of many of the non-*Classopollis* pollen, as well as spores, corroborate the suggestion of a significantly warm climate indicated by the consistent superabundance of *Classopollis* spp.

The proliferation of land plants that were adapted to a warm and dry climate suggests drier conditions throughout the Early Toarcian, in the hinterland of the palaeo-Sichuan Basin. Previous study based on sedimentary evidence from the Da'anzhai Member, e.g. backshore reddish mudrocks with calcisols, lacustrine micritic dolomites and/or gypsum, also suggests that aridification could be most intense during the Toarcian in the Sichuan Basin, despite that the Da'anzhai Member was deposited during the largest lacustrine transgression period (Li et al., 2020). The organic macerals, such as fusinite, semifusinite and pyrofusinite typically formed from combustion, possibly during extensive wildfires, and are more abundant in the lower part of the Da'anzhai Member in Core A (Table 1). This stratigraphic position suggests overall dryer and more fire-prone climatic conditions prior to the T-OAE, compared to elevated seasonality as suggested by climate models during the T-

OAE (Loope et al., 2001; Dera and Donnadieu, 2012; Slater et al., 2019), when intensified hydrological cycling led to expansion of the palaeo-Sichuan mega-lake.

Similarly, the late Early Jurassic flora identified in the upper Changliangzi Formation from the Tianshifu Basin in North China Block indicates a dominant warm and humid climate, with related plants accounted for 69%, while drought-resistant plants increased to 10% (Zhang et al., 2020), probably resulted from strong seasonality. At the same time, the basin also experienced a transformation from shallow-lake facies to deep-lake facies, as has been observed from the paleo-Sichuan lake.

6. Conclusions

The thermal maturity of the organic matter in Core A is at the peak oil window, as is indicated by Tmax values, organic petrography, palynology and biomarker parameters. Core B is thermally more mature, so that only limited biomarker investigation was possible. The unusually high abundance of rearranged hopanes in the Da'anzhai Member of Core A was a result of clay-catalyzed diagenetic changes of the organic matter after deposition.

Organic matter in the laminated black-shale interval of the Da'anzhai Member was largely derived from both algal and bacterial biomass that formed when the water level in the palaeo-Sichuan mega-lake was relatively high and geographically more extensive. Organic-matter enrichment in the Da'anzhai Member of the Sichuan Basin mainly resulted from enhanced aquatic primary productivity linked to elevated nutrient supply during periods of intensified hydrological cycling. The reducing/stratified conditions in the water-column and/or sedimentary pore space facilitated the preservation of elevated organic matter flux. This palaeo-depositional environment, linked to global climatic change in response to the development of Early Toarcian super-greenhouse conditions, eventually resulted in the deposition of the organic-rich, algal-dominated black shales of the Upper Da'anzhai Member in the Sichuan Basin at this time. This sedimentary signature suggests a direct negative feedback, in which the initial release of carbon into the global ocean-atmosphere system resulted in climatic and environmental conditions that were preconditioned to enhance carbon sequestration and the formation of the prolific lacustrine hydrocarbon source rocks of the Da'anzhai Member.

The composition of land plants during the early Toarcian in the palaeo-Sichuan lake indicates relatively dry climate in the hinterland preceding the T-OAE, with frequent forest fires. Subsequently, conditions of strong seasonality prevailed, with both dry and wet climate during the T-OAE itself under greenhouse-gas-induced global warming.

Acknowledgements

Shell International Exploration & Production B.V. is thanked for financial support for this study. George Siavalas from Shell Global Solutions International B.V. is acknowledged for taking the organic petrographic photos. Tai-Ran Jiang, Malcolm Dransfield and Xue-Yan Li (Shell China Exploration and Production Co. Ltd.), Erik Tegelaar, Olaf Podlaha, Sander van den Boorn (Shell Global Solutions International B.V.) and Qinggao Zeng and Zhiping Tang (PetroChina Southwest) are gratefully acknowledged for discussions and for providing the sample materials for this study. James B. Riding publishes with the approval of the Executive Director of the British Geological Survey (NERC). This paper is a contribution to IGCP 632 (International Union of Geological Sciences and United Nations Educational, Scientific and Cultural Organization, IUGS-UNESCO), "Continental Crises of the Jurassic: Major Extinction events and Environmental Changes within Lacustrine Ecosystems" and IGCP 655 (IUGS-UNESCO), "Toarcian Oceanic Anoxic Event: Impact on marine carbon cycle and ecosystems."

Figure Captions:

Fig. 1. The extent and location of the palaeo-Sichuan lake. The map on the left shows a regional tectonic plate reconstruction at 179 Ma, with positions of the latest Early Jurassic lacustrine Sichuan, Tarim and Ordos basins marked (Xu et al., 2017). The map on the right illustrates the location of the two cores studied here, within the Sichuan Basin. The relative variations in lake depth are illustrated in blue, with the darker shade representing deeper water areas; the green brickwork representing fossiliferous limestone and the yellow dotted ornament representing deltaic deposits; palaeo-mountain ranges are marked in brown, and the Da'anzhai Member isopachs are also indicated.

Fig. 2. Locations of Core A and Core B in relation to the lithofacies. No cores from the deeper water facies were available for study.

Fig. 3. Chemostratigraphical (carbon-isotope) correlation between Core A and Core B modified from Xu et al. (2017). Carbon-isotope ratios of the bulk organic matter and the long-chain *n*-alkanes are from Xu et al. (2017), and the carbon-isotope ratios in Core A and B of the sample residues after ASE-extraction are from this study. Calcium concentrations are plotted above the combined core photos for both cores to illustrate lithological change, with lighter colours and high Ca% representing limestones, and darker colours and lower Ca% representing shale (Xu et al., 2017). High-resolution TOC and HI records are plotted in grey shading and blue square dots (Xu et al., 2017). Rock Eval parameters, including TOC, HI and PI from the samples that were analysed for molecular biomarker analysis are compared with original whole-rock data in black (full square symbols) and data from sample residues after ASE-extraction in grey (full square symbols).

Fig. 4. Kerogen characterization for Core A: the left figure shows the pseudo-Van Krevelen diagram (HI *versus* OI) (following Delvaux *et al.*, 1990). On the right panel are HI and OI values plotted against depth. Black full circles represent samples with TOC values equal to or above 1 wt. %; black open circles represent samples with TOC values below 1 wt. %.

Fig. 5. Photographs of different macerals from Core A. Photographs A-1 and A-2: *Botryococcus*-derived telalginite close to oil droplets under UV and reflected white light, showing an orange-yellow colour of moderate intensity in the UV light and dark grey-brownish colour in the reflected white light (in oil immersion) (Core A: 2681.17 m); Photograph B: bitumen derived from *Botryococcus* under UV light (Core A: 2691.25 m); Photograph C: sporinite and liptodetrinite in orange colour under UV light (Core A: 2702.13 m); Photograph D: sporinite showing an orange colour under UV light (Core A: 2710.73 m); Photograph E: funginite particle showing a light grey colour under reflected white light (Core A: 2691.25 m); Photograph F: fusinite particle showing high-reflecting light grey colour under reflected white light (Core A: 2710.73 m); Photograph G: semifusinite particle showing grey colour under reflected white light (Core A: 2710.73 m).

Fig. 6. GC/FID traces of the total lipid extracts (TLE) from six samples in Core A and two samples in Core B. The two high peaks in the Core B samples are likely contaminants.

Fig. 7. Chromatogram of *m/z* 191 from GC/MS aligned with panels of mass chromatograms of C_{27}–C_{35} hopanes from GC/MSxMS data, with sample from depth 2681.17 m of Core A as an example. In the GC/MSxMS panels, the different transitions all have the same range for the *x*-axis and are all auto-scaled to the highest peak for the *y*-axis. Abbreviations: EE: early eluting hopane; D: diahopane; H: hopane; Gamm: Gammacerane.

Fig. 8. Mass chromatogram of *m/z* 217 from GC/MS aligned with panels of chromatograms of C_{26}–C_{29} steranes from GC/MSxMS data, with the sample from depth 2681.17 m of Core A as an example. In the GC/MSxMS panels, the different transitions all have the same range for the *x*-axis and are all auto-scaled to the highest peak for the *y*-axis.

Fig. 9. Ratios between the different rearranged hopanes and steranes and the normal hopanes and steranes plotted on the left panel next to the combined core photos with calcium concentrations illustrating the lithological change in Core A (darker colour→shale; lighter colour→limestone). On the right are Tmax and PI plots from Rock Eval pyrolysis that indicate thermal maturity.

Fig. 10. Indicators of redox conditions and biomass changes in Core A, based on Rock-Eval, palynological and molecular biomarker study. Data are representing redox-conditions, water-column stratification, lacustrine biomass, and relative contribution of algal vs bacterial biomass to organic matter.

Fig. 11. Palynomorph occurrence and abundance in Core A plotted against TOC, HI and carbon-isotope records.

Table 1. The qualitative and semi-quantitative (in vol. %) characterization of organic and mineral matter in samples from Core A.

References

Aizenshtat, Z. 1973. Perylene and its geochemical significance. *Geochimica et Cosmochimica Acta*, **37**, 559–567.

Al-Suwaidi, A.H., Hesselbo, S.P., et al. 2016. The Toarcian Oceanic Anoxic Event (Early Jurassic) in the Neuquén Basin, Argentina: A Reassessment of Age and Carbon Isotope Stratigraphy. *The Journal of Geology*, 124, 171–193.

Baker, S. J., Hesselbo, S. P., Lenton, T. M., Duarte, L. V. and Belcher, C. M. 2017. Charcoal evidence that rising atmospheric oxygen terminated Early Jurassic ocean anoxia. *Nature Communications*, **8**, 15018.

Balme, B. E. 1995. Fossil in situ spores and pollen grains: an annotated catalogue. *Review of Palaeobotany and Palynology*, **87**, 81–323.

Batten, D.J. 1975. Wealden palaeoecology from the distribution of plant fossils. *Proceedings of the Geologists' Association*, **85**, 433–458.

Batten, D. J. and Dutta, R. J. 1997. Ultrastructure of exine of gymnospermous pollen grains from Jurassic and basal Cretaceous deposits in Northwest Europe and implications for botanical relationships. *Review of Palaeobotany and Palynology*, **99**, 25–54.

Behar, F., Beaumont, V. and De B. Penteado, H.L. 2001. Rock-Eval 6 Technology: Performances and Developments. *Oil & Gas Science and Technology–Rev*. **IFP 56**, 111–134.

Brassell, S.C., Eglinton, G. and Fu, J.M. 1986. Biological marker compounds as indicators of the depositional history of the Maoming oil shale. *Organic Geochemistry*, **10**, 927–941.

Brazier, J., Suan, G., Tacail, T., Simon, L., Martin, J.E., Mattioli, E. and Balter, V. 2015. Calcium isotope evidence for dramatic increase of continental weathering during the Toarcian oceanic anoxic event (Early Jurassic). *Earth and Planetary Science Letters*, **411**, 164–176.

Brocks, J.J., Love, G.D., Summons, R.E., Knoll, A.H., Logan, G.A. and Bowden, S.A. 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature*, **437**, doi: 10.1038/nature04068.

Cai, C., Worden, R. H., Bottrell, S. H., Wang, L. and Yang, C. 2003. Thermochemical sulphate reduction and the generation of hydrogen sulphide and thiols (mercaptans) in Triassic carbonate reservoirs from the Sichuan Basin, China. *Chemical Geology*, **202**, 39–57.

Carroll, A.R. and Bohacs, K.M. 2001. Lake-type controls on petroleum source rock potential in nonmarine basins. *AAPG Bulletin*, **85**, 1033–1053.

Couper, R.A. 1958. British Mesozoic microspores and pollen grains. *Palaeontographica* Abteilung B **103**, 75–179.

Cranwell, P.A. 1977. Organic geochemistry of Cam Loch (Sutherland) sediments. *Chemical Geology*, **10**, 619–627.

Dejax, J., Pons, D. and Yans, J. 2007. Palynology of the dinosaur-bearing Wealden facies in the natural pit of Bernissart (Belgium). *Review of Palaeobotany and Palynology*, **144**, 25–38.

Delvaux, D., Martin, H., Leplat, P. and Paulet, J. 1990. Geochemical characterization of sedimentary organic matter by means of pyrolysis kinetic parameters. *Organic Geochemistry*, **16**, 175–187.

Dera, G., Brigaud, B., et al. 2011. Climatic ups and downs in a disturbed Jurassic world. *Geology*, **39**, 215–218.

Dera, G. and Donnadieu, Y. 2012. Modelling evidences for global warming, Arctic seawater freshening, and sluggish oceanic circulation during the Early Toarcian anoxic event. *Paleoceanography*, **27**, PA2211.

Derenne, S., Largeau, C., Casadevall, E. and Connan, J. 1988. Comparison of torbanites of various origins and evolutionary stages. Bacterial contribution to their formation. Cause of lack of botryococcane in bitumens. *Organic Geochemistry*, **12**, 43–59.

Didyk, B.M., Simoneit, B.R.T., Brassell, S.C. and Eglinton, G. 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature*, **272**, 216–222.

Duncan, R.A., Hooper, P.R., Rehacek, J., Marsh, J.S. and Duncan, A.R. 1997. The timing and duration of the Karoo igneous event, southern Gondwana. *Journal of Geophysical Research: Solid Earth*, **102**, 18127–18138.

Eglinton, G. and Hamilton, R.J. 1967. Leaf epicuticular waxes. *Science*, **156**, 1322–1335.

Farrimond, P., Eglinton, G., Brassell, S.C. and Jenkyns, H.C. 1989. Toarcian anoxic event in Europe: an organic geochemical study. *Marine and Petroleum Geology*, **6**, 136–147.

Farrimond, P., Talbot, H.M., Watson, D.F., Schulz, L.K. and Wilhelms, A. 2004. Methylhopanoids: Molecular indicators of ancient bacteria and a petroleum correlation tool. *Geochimica et Cosmochimica Acta*, **68**, 3873–3882.

Ficken, K.J., Li, B., Swain, D.L. and Eglinton, G. 2000. An n-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. *Organic Geochemistry*, **31**, 745–749.

Filatoff, J. 1975. Jurassic palynology of the Perth Basin, Western Australia. *Palaeontographica* Abteilung B **154**, 1–120.

Francis, J.E. 1983. The dominant conifer of the Jurassic Purbeck Formation, England. *Palaeontology*, **26**, 277–294.

French, K.L., Sepúlveda, J., Trabucho-Alexandre, J., Gröcke, D.R. and Summons, R.E. 2014. Organic geochemistry of the early Toarcian oceanic anoxic event in Hawsker Bottoms, Yorkshire, England. *Earth and Planetary Science Letters*, **390**, 116–127.

Gorbanenko, O. 2017. A dry polishing technique for the petrographic examination of mudrocks. *International Journal of Coal Geology*, **180**, 122–126.

Gröcke, D.R., Hori, R.S., Trabucho-Alexandre, J., Kemp, D.B. and Schwark, L. 2011. An open ocean record of the Toarcian oceanic anoxic event. *Solid Earth*, **2**, 245–257.

Guo, T., Li, Y. and Wei, Z. 2011. Reservoir-forming conditions of shale gas in Ziliujing Formation of Yuanba Area in Sichuan Basin (in Chinese with English abstract). *Natural Gas Geoscience*, **22**, 1–7.

Hallam, A. 1981. A revised sea-level curve for the Early Jurassic. *Journal of the Geological Society*, **138**, 735–743.

He, F. and Zhu, T. 2012. Favorable targets of breakthrough and built-up of shale gas in continental facies in Lower Jurassic, Sichuan Basin (in Chinese with English abstract). *Petroleum Geology & Experiment*, **34**, 246–251.

Hermoso, M., Callonnec, L.L., Minoletti, F., Renard, M. and Hesselbo, S.P. 2009. Expression of the Early Toarcian negative carbon-isotope excursion in separated carbonate microfractions (Jurassic, Paris Basin). *Earth and Planetary Science Letters*, **277**, 194–203.

Hesselbo, S.P. and Jenkyns, H.C. 1998. British Lower Jurassic Sequence Stratigraphy. *SEPM Special Publication*, **60**, 562–581.

Hesselbo, S.P., Gröcke, D.R., Jenkyns, H.C., Bjerrum, C.J., Farrimond, P., Bell, H.S.M. and Green, O.R. 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature*, **406**, 392–395.

Hesselbo, S.P., Jenkyns, H.C., Duarte, L.V. and Oliveira, L.C.V. 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). *Earth and Planetary Science Letters*, **253**, 455–470.

Hesselbo, S.P. 2008. Sequence stratigraphy and inferred relative sea-level change from the onshore British Jurassic. *Proceedings of the Geologists' Association*, **119**, 19–34.

Holba, A. G., Tegelaar, E., Ellis, L., Singletary, M. S. and Albrecht, P. 2000. Tetracyclic polyprenoids: Indicators of freshwater (lacustrine) algal input. *Geology*, **28**, 251–254.

Houben, A., Goldberg, T. and Slomp, C.P. 2020. Biogeochemical evolution and organic carbon deposition on the Northwestern European Shelf during the Toarcian Ocean Anoxic Event, *Palaeogeography, Palaeoclimatology, Palaeoecology*, https://doi.org/10.1016/j.palaeo.2020.110191

Huang, D., Duan, Y., Li, Y., Chen, H., Yan, W. and Dai, H. 2018. Study on the TOC lower limit of shale oil and gas of freshwater lake facies: a case study on the Jurassic Da'anzhai member in the Sichuan Basin. *China Petroleum Exploration*, **23**, 1–9.

Huang, S., et al. 2020. Biomarker distributions and depositional environments of continental source rocks in Sichuan Basin, SW China. *Energy Exploration & Exploitation*, **38**, 2296–2324.

Huang, W.Y. and Meinschein, W.G., 1979. Sterols as ecological indicators. *Geochimica et Cosmochimica Acta*, **43**, 739–745.

Hughes, W.B., Holba, A.G. and Dzou, L.I.P. 1995. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. *Geochimica et Cosmochimica Acta*, **59**, 3581–3598.

Hutton, A. C. 1987. Petrographic classification of oil shales. *International Journal of Coal Geology*, **8**, 203 – 231.

Ikeda, M., Hori, R.S., Ikehara, M., Miyashita, R., Chino, M. and Yamada, K. 2018. Carbon cycle dynamics linked with Karoo-Ferrar volcanism and astronomical cycles during Pliensbachian-Toarcian (Early Jurassic). *Global and Planetary Change*, **170**, 163–171.

Jeffrey, E.C. and Chrysler, M.A. 1906. The lignites of Brandon. *Fifth report of the Vermont State Geologist*, **6**, 195–201.

Jenkyns, H. C. 1985. The Early Toarcian and Cenomanian-Turonian Anoxic Events in Europe: Comparisons and Contrasts. *Geologische Rundschau*, **74**, 505–518.

Jenkyns, H. C. 1988. The Early Toarcian (Jurassic) Anoxic Event: Stratigraphic, Sedimentary, and Geochemical Evidence. *American Journal of Science*, **288**, 101–151.

Jenkyns, H.C., Jones, C.E., Grocke, D.R., Hesselbo, S.P. and Parkinson, D.N. 2002. Chemostratigraphy of the Jurassic System: applications, limitations and implications for palaeoceanography. *Journal of the Geological Society*, **159**, 351–378.

Jenkyns, H.C. 2003. Evidence for rapid climate change in the Mesozoic–Paleogene greenhouse world. *Philosophical Transactions of the Royal Society of London A*, **361**, 1885–1916.

Jenkyns, H.C. 2010. Geochemistry of oceanic anoxic events. *Geochemistry, Geophysics, Geosystems*, **11**, Q03004, doi: 10.1029/2009gc002788.

Jiang, C., Alexander, R., Kagi, R.I. and Murray, A.P. 2000. Origin of perylene in ancient sediments and its geological significance. *Organic Geochemistry*, **31**, 1545–1559.

Jin, X., Shi, Z., et al. 2020. The Jenkyns Event (early Toarcian OAE) in the Ordos Basin, North China. *Global and Planetary Change*, **193**, 103273.

Kemp, D.B., Coe, A.L., Cohen, A.S. and Schwark, L. 2005. Astronomical pacing of methane release in the Early Jurassic period. *Nature*, **437**, 396–399.

Kiepper, A.P., Casilli, A. and Azevedo, D.A. 2014. Depositional paleoenvironment of Brazilian crude oils from unusual biomarkers revealed using comprehensive two dimensional gas chromatography coupled to time of flight mass spectrometry. *Organic Geochemistry*, **70**, 62–75.

Koopmans, M. P., Köster, J., et al. 1996. Diagenetic and catagenetic products of isorenieratene: Molecular indicators for photic zone anoxia, *Geochimica et Cosmochimica Acta*, **60**, 4467–4496.

Koppelhus, E. B. and Dam, G. 2003. Palynostratigraphy and palaeoenvironments of the Rævekløft, Gule Horn and Ostreaelv Formations (Lower–Middle Jurassic), Neill Klinter Group, Jameson Land, East Greenland. *Geological Survey of Denmark and Greenland Bulletin*, **1**, 723–775.

Li, Y. and He, D. 2014. Evolution of tectonic-depositional environment and prototype basins of the Early Jurassic in Sichuan Basin and adjacent areas (in Chinese with English abstract). *Acta Petrolei Sinica*, **35**, 219–232.

Li, X., Wang, J., Rasbury, T., Zhou, M., Wei, Z. and Zhang, C. 2020. Early Jurassic climate and atmospheric CO_2 concentration in the Sichuan paleobasin, southwestern China. *Climate of the Past*, **16**, 2055–2074.

Liu, J., Cao, J., Hu, G., Wang, Y., Yang, R. and Liao, Z. 2020. Water-level and redox fluctuations in a Sichuan Basin lacustrine system coincident with the Toarcian OAE. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **558**, 109942.

Liu, M., Sun, P., et al. 2020. Organic geochemistry of a lacustrine shale across the Toarcian Oceanic Anoxic Event (Early Jurassic) from NE China. *Global and Planetary Change*, **191**, 103214.

Loope, D. B., Rowe, C. M. and Joeckel, R. M. 2001 Annual monsoon rains recorded by Jurassic dunes. *Nature*, **412**, 64–66.

McElwain, J.C., Wade-Murphy, J. and Hesselbo, S.P. 2005. Changes in carbon dioxide during an oceanic anoxic event linked to intrusion into Gondwana coals. *Nature*, **435**, 479–482.

Metzger, P., Largeau, C. and Casadevall, E. 1991. Lipids and macromolecular lipids of the hydrocarbon-rich microalga *Botryococcus braunii*. Chemical structure and biosynthesis. Geochemical and biotechnological importance. *In*: Herz, W. et al. (eds.) *Progress in the Chemistry of Organic Natural Products*. Springer Verlag, Berlin, 1–70.

Moldowan, J. M., Seifert, W. K. and Gallegos, E. J. 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. *AAPG Bulletin*, **69**, 1255–1268.

Nytoft, H.P., Lutnæs, B.F. and Johansen, J.E. 2006. 28-Nor-spergulanes, a novel series of rearranged hopanes. *Organic Geochemistry*, **37**, 772–786.

Nytoft, H.P., Lund, K., et al. 2007. Identification of an early-eluting rearranged hopane series. Synthesis from hop-17(21)-enes and detection of intermediates in sediments. The 23rd International Meeting on Organic Geochemistry.

Percival, L.M.E., Witt, M.L.I., et al. 2015. Globally enhanced mercury deposition during the end-Pliensbachian extinction and Toarcian OAE: A link to the Karoo–Ferrar Large Igneous Province. *Earth and Planetary Science Letters*, **428**, 267–280.

Percival, L.M.E., Cohen, A.S., et al. 2016. Osmium isotope evidence for two pulses of increased continental weathering linked to Early Jurassic volcanism and climate change. *Geology*, **44**, 759–762.

Peters, K.E. and Moldowan, J.M. 1993. *The biomarker guide; Interpreting molecular fossils in petroleum and ancient sediments*: Englewood Cliffs, New Jersey, Prentice Hall, pp363.

Peters, K.E. 2000. Petroleum tricyclic terpanes: predicted physicochemical behaviour from molecular mechanics calculations. *Organic Geochemistry*, **31**, 497–507.

Peters, K.E., Walters, C.C. and Moldowan, J.M. 2005. *The biomarker guide: Volume 2. Biomarkers and isotopes in petroleum exploration and earth history*. 2rd edition. Cambridge University Press. pp 489.

Pienkowski, G. and Waksmundzka, M._2009._Palynofacies in Lower Jurassic epicontinental deposits of Poland: tool to interpret sedimentary environments. *Episodes*, **32**, 21–32.

Pocock, S.J. and Jansonius, J. 1961. The pollen genus *Classopollis* Pflug, 1953. *Micropaleontology*, **7**, 439–449.

Pocock, S.J. and Jansonius, J. 1969. Redescription of some fossil gymnospermous pollen (*Chasmatosporites, Marsupipollenites, Ovalipollis*). *Canadian Journal of Botany*, **47**, 155–165.

Ryder, R. T. Petroleum Geology of the Sichuan Basin, China: Report on U.S. Geological Survey and Chinese Ministry of Geology and Mineral Resources Field Investigations and Meetings, October 1991. (U.S. Geological Survey, 1994).

Sælen, G., Tyson, R.V., Telnæs, N. and Talbot, M.R. 2000. Contrasting watermass conditions during deposition of the Whitby Mudstone (Lower Jurassic) and Kimmeridge Clay (Upper Jurassic) formations, UK. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **163**, 163–196.

Scheffer, M., Rinaldi, S., Gragnani, A., Mur, L.R. and van Nes, E.H. 1997. On the dominance of filamentous cyanobacteria in shallow, turbid lakes. *Ecology*, **78**, 272–282.

Schouten, S., van Kaam-Peters, H.M.E., Rijpstra, W.I.C., Schoell, M. and Sinninghe-Damsté, J.S. 2000. Effects of an Oceanic Anoxic Event on the Stable carbon isotopic composition of Early Toarcian Carbon. *American Journal of Science*, **300**, 1–22.

Shevchuk, O., Slater, S.M. and Vajda, V. 2018. Palynology of Jurassic (Bathonian) sediments from Donbas, northeast Ukraine. *Palaeobiodiversity and Palaeoenvironments*, **98**, 153–164.

Sinninghe Damsté, J.S., Kenig, F., Koopmans, M.P., Koster, J., Schouten, S., Hayes, J.M. and De Leeuw, J.W. 1995. Evidence for gammacerane as an indicator of water column stratification. *Geochimica et Cosmochimica Acta*, **59**, 1895–1900.

Slater, S.M., Twitchett, R.J., Danise, S. and Vajda, V. 2019. Substantial vegetation response to Early Jurassic global warming with impacts on oceanic anoxia. *Nature Geoscience*, **12**, 462–467.

Srivastava, S.K. 1976. The fossil pollen genus *Classopollis*. *Lethaia*, **9**, 437–457, https://doi.org/10.1111/j.1502-3931.1976.tb00985.x.

Stukins, S., Jolley, D. W., McIlroy, D. and Hartley, A. J. 2013. Middle Jurassic vegetation dynamics from allochthonous palynological assemblages: an example from a marginal marine depositional setting; Lajas Formation, Neuquén Basin, Argentina. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **392**, 117–127.

Suan, G., van de Schootbrugge, B., Adatte, T., Fiebig, J. and Oschmann, W. 2015. Calibrating and magnitude of the Toarcian carbon cycle perturbation. *Paleoceanography*, **30**, PA2758.

Svensen H., Planke S., Chevallier L., Malthe-Sorenssen A., Corfu F. and Jamtveit B. 2007. Hydrothermal venting of greenhouse gases triggering Early Jurassic global warming. *Earth and Planetary Science Letters*, **256**, 554–566.

Tao, S., Wang, C., Du, J., Liu, L. and Chen, Z. 2015. Geochemical application of tricyclic and tetracyclic terpanes biomarkers in crude oils of NW China. *Marine and Petroleum Geology*, **67**, 460–467.

Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R. and Robert, P. 1998. *Organic petrology*. Gehrüder Borntraeger, Berlin, Stuttgart.

ten Haven, H.L., de Leeuw, J.W., Rullkötter, J. and Sinninghe Damsté, J.S. 1987. Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. *Nature*, **330**, 641–643.

Tuo, J., Wang, X. and Chen, J. 1999. Distribution and evolution of tricyclic terpanes in lacustrine carbonates. *Organic Geochemistry*, **30**, 1429–1435.

Tyson, R. V. Sedimentary organic matter: organic facies and palynofacies. (Chapman & Hall, 1995).

Vakhrameyev, V.A. 1970. Range and paleoecology of Mesozoic conifers, the Cheirolepidiaceae. *Paleontologicheskii Zhurnal*, **4**, 12–25.

Vakhrameyev, V. A. 1981. Pollen Classopollis: indicator of Jurassic and Cretaceous climate. *Paleobotanist*, **28-29**, 301–307.

Vakhrameev, V. A. 1991. *Jurassic and Cretaceous Floras and Climates of the Earth* Cambridge University Press.

Volkheimer, W., Rauhut, O.W.M., Quattrocchio, M.E. and Martinez, M.A. 2008. Jurassic paleoclimates in Argentina, a review. *Revista de la Asociación Geológica Argentina*, **63**, 549–556.

Valiela, I., McClelland, J., Hauxwell, J., Behr, P.J., Hersh, D. and Foreman, K. 1997. Macroalgal blooms in shallow estuaries: controls and ecophysiological and ecosystem consequences. *Limnology and Oceanography*, **42**, Part 2: The Ecology and Oceanography of Harmful Algal Blooms 1105–1118.

Van Kaam-Peters, H.M.E., Köster, J., van der Gaast, S.J., Dekker, M., de Leeuw, J.W. and Sinninghe Damsté, J.S. 1998. The effect of clay minerals on diasterane/sterane ratios. *Geochimica et Cosmochimica Acta*, **62**, 2923–2929.

Volkman, J.K. 1986. A review of sterol markers for marine and terrigenous organic matter. *Organic Geochemistry*, **9**, 83–99.

Volkman, J.K. 2014. Acyclic isoprenoid biomarkers and evolution of biosynthetic pathways in green microalgae of the genus Botryococcus. *Organic Geochemistry*, **75**, 36–47.

Wakeham, S.G., Schaffner, C., Giger, W., Boon, J.J. and de Leeuw, J.W. 1979. Perylene in sediments form the Namibian Shelf. *Geochimica et Cosmochimica Acta*, **43**, 1141–1144.

Wang, Y., Fu, B., et al. 2010. *The terrestrial Triassic and Jurassic Systems in the Sichuan Basin, China*. University of Science & Technology of China Press.

Wang, X., He, S., Guo, X., Zhang, B. and Chen, X. 2018. The resource evaluation of Jurassic shale in North Fuling Area, Eastern Sichuan Basin, China. *Energy Fuels*, **32**, 1213–1222.

Welander, P.V and Summons, R.E. 2012. Discovery, taxonomic distribution, and phenotypic characterization of a gene required for 3-methylhopanoid production. *Proceedings of the National Academy of Sciences of the United States of America*, **109**, 12905–12910.

Wilkin, R.T., Barnes, H.L. and Brantley, S.L. 1996. The size distribution of framboidal pyrite in moderm sediments: an indicator of redox conditions. *Geochimica et Cosmochimica Acta*, **60**, 3897–3912.

Xu, W., Ruhl, M., et al. 2017. Carbon sequestration in an expanded lake system during the Toarcian Oceanic Anoxic Event. *Nature Geoscience*, **10**, 129–134.

Xu, W., Ruhl, M., et al. 2018a. Evolution of the Toarcian (Early Jurassic) carbon-cycle and global climatic controls on local sedimentary processes (Cardigan Bay Basin, UK). *Earth and Planetary Science Letters*, **484**, 396–411.

Xu, W., Mac Niocaill, C., Ruhl, M., Jenkyns, H.C., Riding, J.B. and Hesselbo, S.P. 2018b. Magnetostratigraphy of the Toarcian Stage (Lower Jurassic) of the Llanbedr (Mochras Farm) Borehole, Wales: basis for a global standard and implications for volcanic forcing of palaeoenvironmental change. *Journal of the Geological Society*, **175**, 594–604.

Zhang, Q., Gong, E., Zhang, Y. and Guan, C. 2020. Early Jurassic (Toarcian) warming identified from lacustrine sediments of eastern Liaoning, China. Geological Magazine, https://doi.org/10.1017/S0016756820001235

Zhu, Y., Hao, F., Zou, H., Cai, X. and Luo, Y. 2007. Jurassic oils in the central Sichuan basin, southwest China: Unusual biomarker distribution and possible origin. *Organic Geochemistry*, **38**, 1884–1896.

Zou, C. 2013. *Unconventional Petroleum Geology*. Chapter 3. Petroleum Industry Press. 61–109.