Carbon sequestration in an expanded lake system during the Toarcian oceanic anoxic event

Weimu Xu[1]*, Micha Ruhl[1], Hugh C. Jenkyns[1], Stephen P. Hesselbo[2], James B. Riding[3], David Selby[4], B. David A. Naafs[5], Johan W.H. Weijers[6], Richard D. Pancost[5], Erik W. Tegelaar[6], Erdem F. Idiz[1]

[1]Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, UK (*Correspondence: weimu.xu@earth.ox.ac.uk)

[2]Camborne School of Mines, University of Exeter, Penryn TR10 9FE, UK

[3]British Geological Survey, Keyworth, Nottingham NG12 5GG, UK

[4]Department of Earth Sciences, University of Durham, Durham DH1 3LE, UK

[5]Organic Geochemistry Unit, School of Chemistry and Cabot Institute, University of Bristol, Bristol BS8 1TS, UK

[6]Shell Global Solutions International, Rijswijk 2288 GS, The Netherlands

The early Toarcian Oceanic Anoxic Event (T-OAE; ~183 Ma) was marked by marine anoxia–euxinia and globally significant organic-matter burial, accompanied by a major global carbon-cycle perturbation probably linked to Karoo-Ferrar volcanism. Although the T-OAE is well studied in the marine realm, accompanying climatic and environmental change on the continents is poorly understood. Here, we present radiometric, palynological and geochemical data from lacustrine black shales in the Sichuan Basin, China. We demonstrate that a major lake system developed on land coeval with the T-OAE, likely due to enhanced hydrological cycling under elevated atmospheric pCO_2. Increased lacustrine organic productivity from elevated fluvial nutrient supply caused burial of ~360 Gt of carbon in the Sichuan Basin alone, presenting an important negative feedback in the global exogenic carbon cycle. Coeval accelerated organic-carbon burial in both marine and lacustrine basins suggests nutrient delivery as the prime cause for carbon sequestration during the T-OAE.

The early Toarcian Oceanic Anoxic Event (T-OAE at ~ 183 Ma) is recognized as one of the most intense and geographically extensive events of oceanic redox change and accompanying organic-carbon burial in the Mesozoic Era[1,2]. The T-OAE is marked by major changes in global geochemical cycles, with an apparently rapid negative shift of as much as ~7‰ in marine and terrestrial organic-carbon isotope records and a typically smaller (3–6‰) negative excursion in carbonate archives and specific organic compounds[3-10]. The observed early Toarcian perturbation to the exogenic carbon cycle has been linked to volcanism of the Karoo-Ferrar large igneous province (LIP) and associated release of volcanogenic CO_2, thermogenic methane (CH_4) from sill intrusion into Gondwanan coals, and biogenic methane from dissociation of sub-seafloor clathrates[3,6,11-13]. Early Toarcian elevated atmospheric $p$$CO_2$ likely induced climatic and environmental change[5,12,14-16] by accelerating the global hydrological cycle and increasing silicate weathering, thereby increasing delivery of riverine nutrients to the oceans and potentially also to large inland lakes[17]. In the marine realm, the consequential increase in primary productivity and carbon flux to the sea floor has been linked with enhancing the burial of planktonic material in relatively deep continental margin sites, whereas in shallower water semi-restricted marine basins, chemical and physical water-column stratification likely aided the burial of organic matter[17]. Particularly in northern Europe, the evidence points to regional to global development of anoxic/euxinic (sulphide-rich) bottom waters that strongly affected palaeoceanographic conditions and marine ecosystems[15,17,18]. Globally significant burial of ^{13}C-depleted photosynthetically derived organic matter produced an overarching positive carbon-isotope excursion (CIE) interrupted by the characteristic abrupt negative shift that typically characterizes the T-OAE (Early Toarcian *tenuicostatum−falciferum* ammonite biozones)[1,2,18].

Marine records of the T-OAE, based on the presence of apparently coeval organic-rich shales, have now been identified from many outcrops in both the northern and southern hemispheres[2,5], but climatic and environmental change on the continents is still poorly understood. Intriguingly, however, sedimentary archives from continental interiors in China (e.g. the Tarim, Ordos and Sichuan Basins) are consistently marked by the occurrence of organic-rich black shales that are latest Early Jurassic in age[19-21]. This stratigraphical evidence suggests that major inland lakes potentially formed or expanded contemporaneously with the T-OAE. Here, we (1) determine the precise age of the upper Lower Jurassic lacustrine organic-rich black shales in the Sichuan Basin; (2) determine their depositional context; and (3) explore the possible relevance of major lake formation as an additional sink for carbon in the context of the major disturbance in the early Toarcian exogenic carbon cycle.

GEOLOGICAL SETTING OF THE SICHUAN BASIN

The present-day topographic Sichuan Basin covers a total area of ~230,000 km^2, almost three times the size of Lake Superior (82,100 km^2), the most extensive modern freshwater lake in the world[22]. The Early Jurassic Sichuan Basin (and the palaeo-Sichuan lake system) is thought to have been even larger than its present confines[23] (Figure 1). The basin formed on the western part of the Yangtze Platform and sedimentation commenced with the Neoproterozoic Sinian Sequence (850–570 Ma)[24]. Shallow marine carbonates formed from the Tonian 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[24]. 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[22]. Siliciclastic 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 northwestern and northern margins of the Sichuan Basin[21,23–25] (Figure 1). Continental/fluvial deposits and red pedogenic horizons with soil carbonate nodules mark the Ma'anshan Member (middle Ziliujing Formation) and underlie the lacustrine facies of the upper Lower Jurassic Da'anzhai Member (uppermost Ziliujing Formation). The Da'anzhai Member represents the development of, or transition to, continuously lacustrine conditions and the formation of a major lake. 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[26].

AGE AND STRATIGRAPHY

Two cores (Figure 1) were taken from the more proximal, northwestern part of the Sichuan Basin, each penetrating the entire Da'anzhai Member which is ~50−70 m in thickness here. The Da'anzhai Member in both successions exhibits alternating beds of fossiliferous carbonate and a spectrum of mudrocks from clay-rich marl to laminated black shale (Figure 2). Diverse freshwater bivalves, ostracods, gastropods and conchostracans in the fossiliferous carbonate beds and mudstone beds confirm these sediments to be lacustrine deposits[27]. The freshwater ostracod faunal assemblages, which include *Darwinula* spp. and *Metacypris unibulla,* suggest a late Early Jurassic age[28].

The palynomorph content of the lacustrine Da'anzhai Member, with the superabundance of the pollen *Classopollis* sp. (and the absence of *Callialasporites* spp.), the occurrence of the spore *Ischyosporites vaerigatus*, the acritarch *Veryhachium* *collectum*, multi-specimen clumps of the prasinophyte *Halosphaeropsis liassica* and the rare occurrence of the dinoflagellate cyst ?*Skuadinium* sp., is biostratigraphically significant (Supplementary Information Figure S4 with a range chart of selected palynomorphs). The palynomorph assemblages are comparable to floras from early Toarcian marine successions in northern Europe and Australia, and also indicate that the successions studied are of comparable age. The superabundance of the thermophylic pollen genus *Classopollis* and the occurrence of the opportunistic prasinophyte species *Halosphaeropris liassica,* thought to have thrived in environmentally stressed conditions and normally occurring in multi-specimen clumps, are especially typical of the T-OAE (Supplementary Information)[29–32].

Re-Os radiometric dating on 16 samples from two combined intervals of the Da'anzhai lacustrine black shale (Core A) shows a well-constrained single isochron of 180.3±3.2 Ma (Figure 3; Supplementary Information Figure S1), placing the Da'anzhai Member in the Toarcian, following the Jurassic timescale of Ogg and Hinnov (2012)[33]. A Re-Os isochron for the organic-rich marine mudrock from the *falciferum* ammonite subbiozone in Yorkshire, UK suggests a depositional age of 178.2±5.6 Ma[34]. The age obtained here for the lacustrine Da'anzhai Member in the Sichuan Basin thus largely overlaps the Re-Os isochron- based age of the early Toarcian in the marine realm (Figure 3; Supplementary Information Figure S2).

Furthermore, $\delta^{13}C_{TOC}$ analyses of Core A reveal <3‰ fluctuations in the basal 15 m of the Da'anzhai Member, followed by a transient (but possibly stepwise) ~4‰ negative excursion (Figure 2). The base of Core B is interpreted to be stratigraphically higher, and similarly shows a ~4‰ negative excursion in $\delta^{13}C_{TOC}$ (Figure 2), followed by a full positive return to initial base values. Although the two cores penetrate the same lithological unit, they cover slightly different stratigraphical intervals. The two cores combined present the complete negative CIE, which is also similar in shape and magnitude to that observed in marine records of the T-OAE (Figure 3)[6,34]. Compound-specific long-chain *n*-alkane (C_{23}–C_{33}) $\delta^{13}C$ analyses of Core A also show a distinct ~4‰ negative excursion, similar in magnitude to the bulk organic-matter $\delta^{13}C_{TOC}$ from the same stratigraphical interval (Figures 2, 3). Long-chain *n*-alkanes in sedimentary organic matter are typically sourced from terrestrial higher plants or freshwater algae[35] whose isotopic compositions are commonly indistinguishable because lake water dissolved inorganic carbon (DIC) is in isotopic equilibrium with the atmosphere[36]. Consequently, the observed shift in $\delta^{13}C_{n\text{-alkanes}}$ directly reflects changes in the carbon isotopic composition of the atmosphere (lake water DIC) during the Early Toarcian global carbon-cycle perturbation. Odd-over-even predominance in the long-chain (C_{23}−C_{33}) *n*-alkane distribution, typical for terrestrial higher plant leaf waxes or freshwater algal-sourced sedimentary organic matter[35] is, however, not found in Core A (with a Carbon Preference Index of ~1), probably due to its relatively elevated thermal maturity[37]. Importantly, there is no significant correlation between changes in hydrogen index (HI) values (probably reflecting changes in bulk sedimentary organic-matter sources) and $\delta^{13}C_{TOC}$ during the interval with the carbon-isotopic negative excursion, with R^2 values of ~0.4 and ~0.3 in cores A and B, respectively (Supplementary Figure S6), excluding source mixing as the principal cause of the 4‰ negative carbon-isotope shift. The ~2–3‰ carbon-isotope fluctuations in $\delta^{13}C_{TOC}$ in the lower Da'anzhai Member of Core A (2702–2715m in the core) are, however, not repeated in the $\delta^{13}C_{n\text{-alkane}}$ record. This feature may suggest a shift in the dominant sedimentary organic matter source away from freshwater algae to ^{12}C-depleted terrestrial woody organic matter, with similarly low HI-values of <100 mg HC/ gTOC at 2711.4–2712.3m and 2703.5–2706.6m in the lower Da'anzhai Member of Core A (Figure 2).

Overall, relatively enriched $\delta^{13}C_{TOC}$ values in the more proximal Core B may be explained by the larger woody component of terrestrial residual sedimentary organic matter (the ^{13}C-enriched ligno-cellulose component of a plant)[3,38], as suggested indirectly by low HI values (<200 mg HC/ g TOC; Figure 2) and directly by palynological study (with 26–45% wood). In addition, the more proximal core B is thermally more mature, with Tmax values of 430–518°C (Tmax values of core A are 438–460°C). Maturation of kerogen can increase its $\delta^{13}C_{TOC}$ values by 1–2‰, which could have contributed to the offset observed between the organic carbon isotope records of cores A and B[39]. The observed parallel signature in $\delta^{13}C_{TOC}$ and $\delta^{13}C_{n\text{-alkane}}$ in the main phase of the Da'anzhai Member (>2698 m) therefore likely reflects a true perturbation of the global exogenic carbon cycle. It is strikingly similar in shape and magnitude to what is characteristically observed in Lower Toarcian marine calcite and compound-specific marine and terrestrial organic matter records from Europe and elsewhere spanning the T-OAE[4,8–10] (Figure 3).

Together, the microfossil biostratigraphy, palynostratigraphy, Re-Os dating and chemostratigraphy uniquely constrain the formation of the Da'anzhai Member to be time-equivalent with the T-OAE.

DEPOSITIONAL ENVIRONMENT OF THE DA'ANZHAI MEMBER

Terrestrial (fluvial/deltaic and soil) deposits of the Ma'anshan Member in the mid-Early Jurassic Sichuan Basin pass up-section into the lacustrine facies of the Da'anzhai Member. Chemostratigraphical correlation between the more distal Core A and the more proximal Core B, based on elevated total organic carbon (TOC) and HI and the observed $\delta^{13}C_{TOC}$ negative CIE, suggests a diachronous base of the Da'anzhai Member, as defined by the presence of characteristic lacustrine facies lying stratigraphically above palaeosols (Figure 2). The lower half of the Da'anzhai Member in Core A is marked by abundant fossiliferous limestones (with bivalve and ostracod shell fragments) alternating with more clay-rich sediments. This interval is also marked by generally low TOC (~1 %) and HI values (~150 mg C/g TOC), likely suggesting a nearshore depositional environment with low aquatic organic matter productivity and/or preservation. The abrupt transition from palaeosols to fossiliferous limestone at ~2714.85m, followed by the transition to laminated organic-rich black shales at ~2693.40 m in the more distal Core A, and the coeval transition from palaeosols to laminated organic-rich black shales at ~3156.34m in Core B (Figure 2), suggests the rapid expansion and deepening of the lake, with decreased macrofossil carbonate supply. Macrofossils in the regularly occurring limestone beds show variable degrees of orientation and fragmentation and, depending on the horizon, are in life position, or were subjected to local transport and redeposition. The interbedded marls and black shales are interpreted as representing quieter water sedimentation and/or sedimentation inimical to benthic life.

The fossil assemblages from both cores exhibit a predominantly non-marine depositional environment, with the occurrence of freshwater bivalves, lacustrine ostrocods and the freshwater/brackish alga *Botryococcus* (Supplementary Information). However, some intervals in Core A (2684.49 m to 2695.80 m and 2702.49 m to 2710.73 m) contain *in situ* marine palynomorphs such as the acritarch *Veryhachium collectum* and the prasinophyte *Halosphaeropsis liassica* (Figure 2, Supplementary Information). These occurrences suggest pulses of marine incursions into the basin. Significantly, the oldest sediments of the lacustrine Da'anzhai Member studied in Core A are devoid of acritarchs (Figure 2; Supplementary Information), indicating that the lake had already developed before any potential marine incursion took place. Furthermore, the relative abundance of acritarchs in the samples studied shows no positive correlation with TOC or (pyritic) sulphur abundance, indicating that deposition of the most organic-rich sediments and the supply of sulphate was unrelated to a potential marine connection. Sedimentary facies in Europe and elsewhere indicate that the early Toarcian was characterized by a significant marine transgression, culminating in the *falciferum* ammonite biozone[40,41]. Although the Early Jurassic Sichuan Basin was surrounded by compressional mountain ranges in the north, east and west, the palaeo-Sichuan lake system likely formed at sea level and the basin could, therefore, have been temporarily connected to the ocean to the south (Figure 1 and references herein). Overall, however, the abundance of freshwater fossils and palynomorphs, combined with a more radiogenic initial $^{187}Os/^{188}Os$ value of ~1.29, which is significantly higher than Early Jurassic Toarcian marine $Os_{initial}$ values of 0.4−1.0 recorded from Europe[34] (Supplementary Information), points to a dominantly lacustrine environment during Da'anzhai Member times. This interpretation is further supported by the presence of tetracyclic polyprenoids (TPP), the near absence of C_{30} steranes (typically sourced from marine algae) and high hopane over sterane biomarker ratios throughout Core A[42,43] (Supplementary Information).

The consistent superabundance in both cores of the thermophylic pollen genus *Classopollis*, which is thought to have derived from gymnosperm conifers dwelling in regions marginal to bodies of water, suggests higher temperature conditions in the continental interior or along the shorelines of the palaeo-Sichuan lake system. Elevated atmospheric and marine temperatures during the T-OAE have also been suggested from coeval marine records, also with increased abundance of *Classopollis* and the ^{18}O-

depleted signature of macrofossil calcite[14,18,44]. Previous study of a section from Bornholm, Denmark suggested a sharp increase of atmospheric *p*CO2 reconstructed from terrestrial leaf stomatal density at the onset of the negative CIE[12]. The increased occurrence of *Classopollis* in tetrads (relative to single specimens; Figure 2) observed during the negative CIE interval suggests stressed environmental conditions on land during the T-OAE, likely in response to enhanced atmospheric pCO_2 and greenhouse-gas-induced climatic warming[12,14,18,44,45].

The Toarcian mid-palaeolatitude setting and geomorphology of the palaeo-Sichuan Basin, with surrounding high mountain ranges[21], may have made the basin susceptible to an enhanced monsoonal system and increased hydrological cycle, particularly when warm shallow transgressive seas approached (cf. the modern South Asian monsoon[46]). The formation or strong expansion of the palaeo-lake system in the early Toarcian Sichuan Basin, with the deposition of the Da’anzhai Member lacustrine black shales with elevated TOC (of up to ~3.3%) and HI (of up to 450 mg HC/g TOC) levels, suggests increased aquatic primary productivity, hypothetically due to increased continental weathering and accelerated riverine nutrient supply. Significantly, based on all the stratigraphical data herein (Figure 3), the level of maximum TOC enrichment in the Da’anzhai Member developed coevally with the organic-rich black shale in marine sections from Yorkshire, UK (Figure 3), consistent with a fundamental global climatic control on the introduction of nutrients into aquatic environments, even though the quantity and type of organic matter deposited and preserved may have been different.

Elevated sulphur concentrations in the most organic-rich sections of laminated black shale of the Da’anzhai Member in core A (Figure 3; Supplementary Information), coincide with the occurrence of small (<5 μm diameter) fragments of pyrite and larger framboidal pyrite (Supplementary Information Figure S7). The source of sulphur is, however, as yet uncertain, but lake sulphate could originate from the weathering of the Lower–Middle Triassic evaporites in the hinterland[22]. Although the larger pyrite framboids could have formed diagenetically in sulphide-rich sedimentary pore-waters, the smaller framboids (<5 μm) likely formed by sulphate reduction in the water column, as typically happens under euxinic conditions[47]. The stratigraphical intervals with high (pyritic) sulphur concentrations coincide with levels of elevated sedimentary molybdenum enrichment (with Mo >20 ppm; Figure 3). In oxic conditions, Mo exists as soluble molybdate (MoO_4^{2-}) that adsorbs onto Mn-oxides and only slowly precipitates. In sulphidic (euxinic) waters, however, molybdate dissociates into thiomolybdate anions, which are rapidly reduced to highly reactive Mo(IV) sulphides that precipitate out of solution, leading to sedimentary Mo enrichment[48]. Furthermore, water-column stratification, which is a likely prerequisite for sustained euxinia, is also supported by elevated levels of gammacerane in the black shale interval of Core A (Figure 2; Supplementary Information). Gammacerane is a biomarker derived from tetrahymanol that forms in abundance under conditions of high bacterial productivity within stratified water columns, often in lakes or isolated marine basins[49]. Taken together, the geochemical and mineralogical data suggest the development of a physically or chemically stratified water column when laminated black shales formed in the palaeo-Sichuan Lake, even in relatively proximal depositional settings.

LACUSTRINE CARBON BURIAL AND THE TOARCIAN CARBON CYCLE

The early Toarcian negative CIE has been widely attributed to the release of ^{13}C-depleted volcanogenic CO_2 and/or methane from either thermal metamorphism of Gondwanan coals or the dissociation of sub-sea-floor gas hydrates, also resulting in enhanced early Toarcian atmospheric pCO_2 levels[3,11,12,15]. The typical early Toarcian

$\delta^{13}C$ pattern, with a stepped negative shift interrupting an overarching positive excursion, has been observed in marine and terrestrial organic matter and shallow-water platform and deep-water pelagic carbonates and manifestly affected the entire ocean–atmosphere system[3,5,6,8]. The overall positive shift is attributed to globally accelerated organic-carbon burial whereas the superimposed stepped negative shift suggests that the release of isotopically light carbon took place in pulses that have been attributed to Milankovitch forcing of the global carbon cycle[6]. Astronomical interpretation of periodic fluctuations in chemical and physical proxy records estimate the duration of the early Toarcian negative CIE at 300−900 kyr[6,50–52].

In the Early Toarcian Sichuan Basin, the laminated black shale interval in both cores is marked by elevated HI and TOC values (with HI up to 450 mg HC/g TOC and TOC up to 3.3% in the more distal core A), likely reflecting increased algal primary productivity, in addition to a background supply of terrestrial organic matter, during the interval with the lowest carbon isotope values of the negative CIE. This chemostratigraphical pattern is very similar to that developed in marine sections from northern Europe, where sedimentary TOC-levels can locally reach ~20%. Box-model studies for the early Toarcian carbon cycle suggest that the release of ~9000 Gt carbon from methane clathrates (with $\delta^{13}C$ of ~-60‰) or ~25,000 Gt carbon as thermogenic methane (with $\delta^{13}C$ of ~-35‰), is required to generate a negative $\delta^{13}C$ excursion compatible with the mean change in bulk carbonate of 4–6‰, and which would have caused an increase in atmospheric pCO_2 of ~1000 ppm[7,8,15,53]. Excess atmospheric CO_2 is assumed to have been sequestered both by enhanced weathering of Ca-Mg silicates due to greenhouse warming, and by massive burial of organic carbon in marine dysoxic, anoxic and euxinic depositional environments. These combined processes would have dictated the pattern of $\delta^{13}C$ recovery, but the total amount of ^{13}C-depleted carbon released may have been even larger than modelled because enhanced ^{12}C-enriched carbon burial would have acted as a mechanism to potentially increase ocean-atmosphere $\delta^{13}C$ during the onset of the T-OAE, even though the resultant summed effect was to move values in the opposite direction.

Sequestration of carbon in marine basins is generally considered to have been a major driver behind $\delta^{13}C$ recovery. The sheer size of the latest Early Jurassic continental basins, and the expansion of this major lake in response to Early Toarcian climatic (and possibly sea-level) change, however, provides an additional, and significant, sink for carbon. The Da'anzhai Member lacustrine black shale formed over 70,000 km^2 in the palaeo-Sichuan Basin, with an average thickness of 60−120m and 0.8−3.5% TOC; lacustrine marls and carbonates accumulated coevally over large parts of the remaining 160,000 km^2 of the basin[25]. Applying the average of these parameters, it is estimated that ~360 Gt of carbon was extracted from the global ocean–atmosphere system and sequestered in the palaeo-Sichuan lake during deposition of the early Toarcian Da'anzhai Member black shales alone (Supplementary Information). This figure is, however, a conservative estimate because original sedimentary TOC values may have been even higher considering the present-day maturity of the rock. Also, TOC values in the deepest, most central part of the basin may have been more elevated then in the more proximal cores which were studied here. Assuming the (pulsed) release of 9,000 Gt of carbon from methane clathrates (with a $\delta^{13}C$ of ~-60‰) or 25,000 Gt as thermogenic methane (with a $\delta^{13}C$ of ~-35‰) to explain the observed step-wise negative shift in $\delta^{13}C$ (-5‰; from 1‰ to -4‰) during the T-OAE[53], and assuming carbon sequestration largely by organic-matter burial (with a $\delta^{13}C$ of -25‰) to explain the observed recovery in global $\delta^{13}C$, a simple mass-balance model indicates that early Toarcian carbon burial in the black shales of the palaeo-Sichuan Basin alone sequestered 1.0−1.7% of the total amount sequestered to recover from the $\delta^{13}C$ negative shift during the T-OAE negative CIE (Supplementary Information). The present-day global lake surface area is about ~0.69% of the surface area of the global ocean; lakes, however, account for ~10% of the global carbon drawdown and burial[54]. The palaeo-Sichuan lake alone covered ~230,000 km^2, which is twice the size of England and ~10% of the present-day global lake surface, but it was responsible for, at least, 1.0–1.7% of the global carbon burial flux. The generation of massive sinks of carbon in Early Toarcian continental interiors by the formation and/or expansion of major lakes and subsequent significant sequestration of carbon, in addition to marine carbon burial, potentially significantly impacts the nature and duration of the observed exogenic carbon cycle perturbation. If the carbon sink of the Sichuan Basin black shale had not formed, and with the assumption of constant climatic/environmental parameters affecting the rate of carbon drawdown, the recovery from the $\delta^{13}C$ negative shift would have required an additional ~3,000–16,000 yr of global marine carbon drawdown (Figure 4; Supplementary Information). Given that several other lacustrine basins, for example, the Tarim and Ordos Basins in northwestern and central northern China (Figure 1) also appear to have developed in the late Early Jurassic with the deposition of organic-rich sediments[19,20], these figures are unequivocally minima.

These results suggest an as-yet unidentified negative feedback in the global exogenic carbon cycle during oceanic anoxic events. Climatic warming induced by addition of greenhouse gases to the atmosphere, and an associated increase in hydrological cycling, allowed for the formation of major lake systems in continental interiors, where enhanced fluvial nutrient supply with increased productivity and preservation could have lead to major carbon sequestration. Together with widespread burial of organic matter in the marine realm, the lacustrine carbon sink would have reduced atmospheric pCO_2, allowed rebound of the global $\delta^{13}C$ signal, and cooled global climate through an inverse greenhouse effect[18].

Supplementary Information is included.

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Author contribution statement

W.X., M.R., H.C.J. and S.P.H. designed the project. W.X. and M.R. performed core description and sampling. W.X., M.R., J.B.R., D.S., J.W.H.W. and B.D.A.N. performed geochemical and palynological analyses. All authors contributed to data analysis and interpretation and writing and/or refinement of the manuscript.

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[2.1] RE-OS GEOCHRONOLOGY

Figure S1. Re-Os isochrons. (a) Isochron from samples in the interval between 2692.31 m and 2693.26 m; (b) Isochron from samples in the interval between 2676.87 m and 2677.79 m; (c) combined isochron from all the samples.

Figure S2. Stratigraphical comparison of the Re-Os ages of the marine Jet Rock in Yorkshire (Cohen et al., 2004) and the lacustrine Da'anzhai Member in this study, relative to the 2012 Geological Time-Scale (Gradstein et al., 2012). The two records are aligned with reference to the negative CIE. The light grey shades represent the stratigraphical intervals from which the samples, used for Re-Os dating, were obtained.

[2.2] PALYNOLOGY

Figure S3. Photomicrographs of selected palynomorphs.

Pollen:

1. Two tetrads of *Classopollis*. 2693.35m Core A. BGS sample MPA 66166/slide 3 at S57/2.
2. *Classopollis* spp. 3094.58m Core B. BGS sample MPA 66168/slide 1 at K39.
3. *Classopollis* spp. 3094.58m Core B. BGS sample MPA 66168/slide 1 at K39.

Spore:

4. *Ischyosporites variegatus* (Couper 1958) Schulz 1967. 2693.35m Core A. BGS sample MPA 66166/slide 3 at S63/4.

Aquatic palynomorphs:

5. A clump of the spherical prasinophyte *Halosphaeropsis liassica* Mädler 1963. 2693.35m Core A. BGS sample MPA 66166/slide 3 at C60/3.
6. *Veryhachium* sp. 2693.35m Core A. BGS sample MPA 66166/slide 3 at E55/4.
7. *Micrhystridium* sp. 2702.49m Core A. BGS sample MPA 66167/slide 1 at O62/3.
8. *Micrhystridium* sp. 2693.35m Core A. BGS sample MPA 66166/slide 4 at M66/4.
9. *Veryhachium collectum* Wall 1965. 2702.49m Core A. BGS sample MPA 66167/slide 1 at R65/1.

Figure S4. A range chart of selected palynomorphs. This chart illustrates the known semi-quantitative stratigraphical extents of ten selected palynomorph genera and species that were recorded in this study in order to demonstrate the age-diagnostic nature of these forms. These data form part of the basis for the age model in this study and complement Re-Os radiometric age dating and carbon-isotope stratigraphy. The information herein was compiled from works cited in the bibliography.

[2.3] BIOMARKER ANALYSES

Figure S5. Examples of gammacerane and TPP biomarker spectra from core-depth 2677.5m in Core A.

[2.4] $\delta^{13}C$ *vs.* HI &TOC

Higher plants or marine or freshwater algae fractionate carbon isotope differently during photosynthesis, partly also depending on environmental background conditions (e.g. atmospheric and aquatic pCO_2). Hydrogen indices (HI) vary depending on the organic matter precursors as well as subsequent thermogenic or biogenic degradation. A change in sedimentary organic matter source may thus be reflected by a change in HI values and (possibly) result in a change in bulk organic $\delta^{13}C$. A correlation between HI values and $\delta^{13}C_{TOC}$ in a sedimentary record may therefore reflect organic matter source mixing, rather than a perturbation of the global exogenic carbon cycle. The cores A and B from the Sichuan Basin studied here show no strong correlation between $\delta^{13}C_{TOC}$ and HI values (or TOC), especially not if one considers the interval of the negative carbon isotope excursion (CIE) as illustrated in red in Figure S6 (with an R^2 value of only 0.41). The lack of a clear correlation between possible changes in organic matter sourcing (possibly reflected by changing HI values) and $\delta^{13}C_{TOC}$ suggests that the observed negative CIE likely reflects a true change in the global carbon cycle. This is further supported by the compound-specific carbon isotope analysis on long-chain *n*-alkanes, sourced from terrestrial higher-plant leaf waxes or freshwater algae, which shows a 3–4‰ negative excursion, similar in magnitude as observed in coeval marine successions[75–77]. Aquatic and terrestrial organic matter (e.g. algae, pollen and spores and waxy leaf material) constitutes high HI values, but woody organic matter results in low HI values. Woody organic matter generally also displays a more positive carbon isotopic composition. Therefore, sediments constituting low HI values (indicating more woody sedimentary organic matter) may also be characterized by more positive carbon-isotope values. Core B shows overall low HI values, suggesting a larger proportion of woody sedimentary organic matter, explaining the overall more positive signature in bulk $\delta^{13}C_{TOC}$. The cross-plot between $\delta^{13}C_{TOC}$ and HI of Core B does not show a correlation (with a R^2 of 0.31). However, it still shows the pronounced 4–5‰ negative excursion as observed in Core A. The apparent correlation between HI and bulk $\delta^{13}C_{TOC}$ in Core A, when considering all samples from within and preceding the negative CIE, is likely resulted from possible organic matter source mixing in the Lower Da'anzhai Member (preceding the negative CIE). The several per mille fluctuations in bulk $\delta^{13}C_{TOC}$ in this interval in Core A, are not reflected in the $\delta^{13}C_{n\text{-alkanes}}$ record and are, therefore, unlikely to reflect global carbon-cycle change.

Figure S6. This figure shows the cross-plot relationships between bulk organic $\delta^{13}C$ and Hydrogen Index (HI), and bulk organic $\delta^{13}C$ and Total Organic Carbon (TOC). Specifically, bulk organic $\delta^{13}C$ within the negative CIE from Core A is marked in red.

[2.5] SCANNING ELECTRON MICROSCOPY (SEM)

Figure S7. Examples of pyrite framboids from 2680.4 m (a, b, c) and 2713.12 m (d) in Core A, imaged with a back-scattered electron beam detector. (a) Pyrite likely generated by pore-water sulphate reduction due to the oxidation of organic matter. (b) Small (<5 μm) pyrite framboids may have formed in a euxinic (sulphide-rich) water-column. (c) Fully pyritized shell fragment surrounded by small pyrite framboids. (d) Larger (>5 μm) pyrite framboid, possibly formed during early diagenesis.