

# **Black shale deposition during Toarcian super-greenhouse driven by sea level [submitted to *Climate of the Past*]**

**By**

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## **CUMULATIVE RESPONSES TO THE REFEREES**

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Referee's comments are in *black and italic*

Our responses are in **blue** and preceded by the sign >

Changes in the revised manuscript will appear in **red**

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### **Anonymous Referee #1**

*The manuscript argues for a changing sea level as a primary driver for the local redox conditions using geochemical proxies in concert with sequence stratigraphy during the T-OAE. Constraining sea-level coupled to local redox shifts during major carbon burial events is important for understanding the links and mechanism(s) for initiation, duration and termination. The current state of the manuscript sufficiently explains the proxies and their importance. However, I believe there are portions/sections that could be clarified and/or streamlined to make the manuscript flow more smoothly. Such as, re-arranging the discussion-results section with all of the geochemical data and discussion together and the sequence stratigraphy lumped together will be more logical.*

*Lastly, I would like to see the redox geochemical story tied together a bit better. Where V is high but Mo is low what does this mean?*

> We agree with the fact that redox sensitive markers have not been really integrated in the original submission. In our revision, we have now bridged the sea level part and the geochemistry, and especially making clearer how redox sensitive elements (Mo, V) were influenced by changes in relative sea level. We have completely reorganised the corresponding part (3.3) of the manuscript, and merged the discussion on V/Al, Fe/Al and Mo/TOC in a more coherent way. The ratios are discussed and compared to each other following a stratigraphic order (by black shale intervals). We acknowledge that the manuscript now contains a more logical discussion.

*What are the redox sequences, why are they not observed in Mo?*

> To address this question, a duration for these cycles would have to be established first. As we did not attempt spectral analysis on our trace metal data, we are unable to tackle this question. However, we have no doubt that our paper, and the dataset provided as Supplementary Material, will stimulate subsequent studies performed by cyclostratigraphers. The absence of cyclicities in the Mo record is likely attributable to a longer residence time of Mo in seawater with respect to V and Fe. This point has been added in our revisions (penultimate paragraph of the discussion).

*The figure uses “widespread anoxia” but I think euxinia should be used as these are different depositional settings.*

> We have changed “Widespread Anoxia” for “*Widespread Anoxia / Euxinia?*” on Fig. 4 and in the body text with reference to the appreciable content of pyrite that could indeed testify for euxinia.

*Page 4366 Line 1: Oceanic Anoxic Event does not need to be capitalized and the same for subsequent accronyms (TOC and CIE)*

> Done.

*Line 8: Replace studied to study*

> Done.

*Line 8: Replace stratigraphy to stratigraphic*

> Done.

*Line 20: Atmosphere-Ocean does not need to be capitalized*

> Done.

*Page 4367 Line 14: In principle, I agree with the author regarding the Neuendorf et al., black shale definition; however, inherently there are flaws with using lamination alone to define black shales. The word black shale refers to an organic-rich fine grained sediment while laminations imply something about redox conditions and the ecology. Therefore, the TOC content is important for defining these samples are relatively rare in the geologic record. For example, if there was low oxygen bottom waters in the middle of the low productive Pacific gyres it could be imagined these settings would be laminated but due to low TOC they would not be black. Is it possible to combine laminated and a TOC value (i.e. 1%) for the definition.*

> In fact, this would not change the repartition of our discrete black shale intervals. A prerequisite for defining a black shale facies is indeed lamination of sediment. There are a

number of factors that can modulate the %TOC of black shale such as dilution by carbonate or the detrital fraction. Therefore, a precise limit in %TOC may appear arbitrary (including that proposed by Neuendorf). However, as pointed out in the text, all these black shale intervals have TOC greater than 2%. This organic carbon concentration seems a reasonable definition as 2% is greater than background TOC levels outside the black shale intervals.

*Page 4368 Line 3: A companion? It is more of a precursor to the OAE.*

> We agree. This has been changed.

*Line 5: 'probably reflecting injection of isotopically-light carbon' – due to the negative shift there has to be an injection of light carbon. Unless I am missing something in this sentence 'probably' should be removed.*

> 'probably' has been removed.

*Line 15: 'decisive arguments' I would prefer provided evidence to support or something similar.*

> This has been changed for “has provided invaluable information on the record of the negative CIE and its relation with the T–OAE”.

*Page 4369 Methods – Were there any international standards run? What are the reproducibility, detection limit and error of each metal using the XRF.*

> As mentioned in the manuscript, we measured 9 certified standards provided by Niton Ltd. UK. A short paragraph has been added in our revised manuscript for the reproducibility and limits of detection for each element. For all major elements (Al, Si, Zr and Ti), the typical error associated to the measurement is less than 5% based on replicated standards. For Mo and V, the error is greater and depends on the TOC content. The Limits of Detection for these elements are ~5 and 15 ppm, respectively. The error is in the order of 10%. Mo is not detected when TOC is less than 2%. We have added these points in the Methods paragraph (part. 2).

*How were pyrite concentrations quantified? What is the accuracy?*

> The concentration of pyrite was determined by XRD using the area of the main peak (200). The minimum amount of pyrite detected from peaks (200) on XRD spectrum was in the order of 0.5%. As pyrite has a high diffraction potential ( $I/I_{corr} = 1.6$ ), the error associated to the measurement is rather small, typically less than 5% as now pointed out in the manuscript (2. – second paragraph).

*If there is new data in this manuscript there needs to be a brief description for TOC, TIC and  $\delta^{13}C$  but if this is all from Hermoso et al. (2012) then this portion of the methods should be cut.*

> There are indeed new isotope data (>50 samples) in the present manuscript (below 368m and above 337m). We have added a short description of the methods used in the revised draft in addition to the reference (last paragraph of section 2.).

*Page 4370 Just because Sc1 is not laminated does not mean it was not originally deposited under reducing conditions then slightly oxygenated to allow for some bioturbations (Boyer et al., 2011).*

> Sc 1 is laminated. The non-laminated interval containing 3%wt TOC is a thin interval recorded with the first step as the CIE, i.e. prior to Sc1. We appreciate that this confusion may come from a graphical vagueness in Fig. 2. Therefore, we have changed the representation of this interval on this figure. The presence of *Chondrites* burrows within this interval testifies for bottom water restricted O<sub>2</sub> levels (i.e. no full bottom water anoxia). This has been clarified in the revision (third paragraph of 3.4).

*I am following your argument of oxygenation at the termination of Sc1 due to bioturbation, low pyrite, low TOC. I don't follow the carbonate argument, please explain. How is a change in sedimentation and basinal restriction not considered? I do not believe these changes are completely dictated by sedimentation rates (slower – allowing for deeper oxygen penetration depths – affecting all of these proxies) but this should be addressed. Basin restriction could affect the amount of reactive Fe therefore controlling the pyrite concentrations.*

> This is true. Basinal restriction being intimately associated to sea level, we attributed episodes of enhanced preservation of organic matter to a sea level driver factor (see also last response to Referee#2 on this matter). A sentence has been added to account for this physiographical relationship (last paragraph of discussion).

*Line 18: in average should be replace to on average*

> Done.

*Page 4373 Line 17: “A sharp subsequent decrease in V/Al subsequently although pCO<sub>2</sub> remained continuously high (McElwain et al., 2005; Hermoso et al., 2012)” I am not following this sentence/argument.*

> We have reformulated this sentence, which was indeed a bit confusing. “During this diminution in TOC content and V/Al ratios, the pCO<sub>2</sub> remained high, indicating that diminished DIC levels cannot explain the termination of the black shale interval Sc1 (McElwain et al., 2005; Hermoso et al., 2012)”.

*Page 4375 Line 10: Be explicit when making this statement as I believe you are stating there is no shift in the redox deposition across Sc1 and Sc2 but you have already stated there was a brief oxygenation between the events.*

> Indeed, the sediments show bioturbation at the transition.

*Generally comments I would argue the paper is in need of a paragraph in the intro discussing the timing and event of this OAE for these 'steps' during the OAE.*

> A couple of sentences on this specific point has been added, as it represents a key feature of our study. *"The conjunction of a long-term event, the T-OAE that was recorded during three ammonite Zones, and a rapid and transient carbon isotope perturbation, the T-CIE that lasted less than 500 kyr (Kemp et al., 2011) represents an invaluable archive to unravel the Jurassic Earth's system dynamics"*.

*Generally, the higher Fe/Al during Sc2 and Sc3 values are driven by lower Al concentration rather than an increase in Fe contents which also affect the magnitude of the V ratio but controlling it. This seems rather important and is this due to changing sources of the sediments?*

> This is correct. Enhanced dilution by clay minerals with accompanying higher Al concentrations explains lower Fe/Al and V/Al ratios. However, with available data, we do not have direct evidence for any change in the detrital source.

*Caution must be used when using Mo/TOC ratio alone to interpret the global nature of an event as the modern Black Sea shows low Mo/TOC values while the surface water is similar to the open ocean which is partially driven by its restricted nature. Similarly, this could be argued for any given section but there are multiple sites showing similar Mo/TOC values (this need to be very clear).*

> Mo/TOC profiles across the T-OAE in NW European seaways seem to be comparable. The Yorkshire record (Pearce et al., 2008), NE Paris Basin (Lézin et al., 2013) and Sancerre all record the same trends. This comment is much welcomed as it reinforces our conclusion. A sentence stating this correlation has been added in the new draft (fifth paragraph of 3.4).

*Figures The symbol for burrows is very difficult to see.*

> Done. Also, we will request the Figures to appear largest (page width) compared to what they look like in the peer-reviewed version.

*The labels for the OAE and intervals (Sc and Mb) are very difficult to read.*

> Another means to indicate them has been adopted in Figure 2.

*d18O was not discussed until the 2nd to last paragraph and was previously published. I do not see a reason to include this data if there is no discussion prior to the final few sentences.*

> We think that  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are an indivisible dataset. Although oxygen isotopes and temperatures are not the primary topic of our study, further examination of the T-OAE may require this data. Furthermore,  $\delta^{18}\text{O}$  data are mentioned several times throughout our

manuscript. Therefore, we feel like we should keep these data in the Figure.

## **Anonymous Referee #2**

*The study by Hermoso and colleagues addresses the question of Toarcian black shale deposition in shallow shelf-sea environments. In particular they intend to decipher principle mechanisms for the formation of oxygen deficiency in shelfal waters during and after the Toarcian oceanic anoxic event (T-OAE) as it is defined by the carbon isotope excursion (CIE). By using sedimentary, mineralogical, stable isotopic and elemental concentration proxy records from the Sancerre core in the Paris Basin they suggest relative sea level changes and consequently water depth as a primary prerequisite to establish anoxic conditions in deeper parts of the basin. One result of the study is the geochemical characterization of four distinct laminated organic-carbon rich horizons, with the lowest one (Sc1) corresponding to the negative CIE of the T-OAE. Furthermore, the authors reconstruct relative third-order sea-level by changes based on fluctuations of the  $Q_z/Q_z+Clay$  ratio. The interplay between climatic and sea-level forcing on the formation of shelf-sea anoxia is still not fully understood. In this context this study provides interesting new aspects to the discussion. However, the data interpretation is too focused on sea level change alone and the applied proxies are not sufficiently discussed in detail.*

> As also recommended by Referee #1, we have strengthened our discussion on the interplay between sea level and the discussion on the evolution of redox sensitive elements.

*At first, one aspect that strikes me is the definition of the T-OAE which differs from that of other studies. I cannot see from the presented TOC and carbon isotope data, why the onset of the T-OAE is placed at the base of the tenuicostatum Zone and not at the base of the first black shales which appears to be synchronous to the negative CIE in European basins. The authors argue with a first small organic rich bed of 3 % TOC which, however, is not visible in the lithological log, in the TOC or the  $\delta^{13}C$  data in Figures 2, 3 and 4. For consistency, it would be useful to adopt the definition of previous studies (e.g. Hesselbo et al. 2000 or Harazim et al. 2013) or to provide a robust discussion for such an early commencement of the T-OAE.*

> The onset of the T-OAE is not stratigraphically well-defined in the literature. The **T-OAE** reflects a period of global organic carbon burial that was promoted by intense primary productivity and subsequent  $C_{org}$  burial owing to oxygen-depletion of bottom waters. Hence, the geochemical manifestation of this event is the long-term **positive** trend in carbon isotopes as observed for all other OAEs of the Mesozoic. Within the T-OAE, a major negative **CIE** reflects injection of  $^{12}C$ -rich carbon into the atmosphere-ocean system (via clathrates, volcanism or other means). The authoritative review paper by Jenkyns in G-cubed (2010) makes this point clear: “The early Toarcian OAE has a broadly similar pattern of a positive excursion with an abrupt negative “bite” in its central portion” (quotation now in the manuscript). Hence, reducing the T-OAE to the stratigraphic interval containing the negative CIE (as done in Harazim et al., 2013) is not only erroneous, but also “isotopically”

contradictory. Furthermore, nowhere in Hesselbo et al. (2000), is the T-OAE defined as the position of the negative CIE. Woodfine et al. (2008) have also used the  $\delta^{13}\text{C}$  positive shift as the T-OAE interval in the *tenuicostatum* Zone. However, for the sake of clarity and to avoid any confusion, we have changed several occurrences of the definition of the T-OAE making clear we use the positive  $\delta^{13}\text{C}$  shift in the text now so that we are more “factual”. There is a new paragraph in the introduction discussing this.

*A second issue is the application of the Qz/Qz+Clay ratio as proxy for relative sea-level change. 3rd order sequence stratigraphic boundaries are detected based on the assumption that the Qz/Qz+Clay ratio is a proxy for change in grain size change and that all of the Qz is of detrital origin. However, enrichment in Qz can also be related to siliceous bioproductivity. Without an independent calibration of the Qz/Qz+Clay ratio with grain size I would questioning the reliability of this proxy.*

> The Referee raises here a potential problem in our method in generating a sequence stratigraphy. Especially, s/he questions whether “%Quartz” accounts for detrital mineral only. Siliceous productivity may, indeed, challenge our approach but only if present in our sediments. It should have been stated in our method description that Toarcian NW European have no diatoms (as they appeared in the Late Jurassic), and no radiolarians in the proximal environment of the Paris Basin (De Wever and Baudin, 1996). As there was very limited benthic life during the T-OAE, there are no sponge spicules either in these sediments. Examination of a considerable number of smear slides and SEM preparations for previous studies on this core material since 2009 have never revealed any siliceous biominerals. All above demonstrate that siliceous bioproductivity cannot represent a bias in our method. The quartz content only corresponds to detrital input either as sand or silt grains. It allows using the Qz/Qz+clay index as a proxy for the relative proportion of coarse versus fine detrital material. Our manuscript now states this point for clarity, and we thank the referee for spotting this (third paragraph of the Methods).

*My doubts are supported by the lack of correlation with the detrital element ratios Si/Al, Ti/Al and Zr/Al. While the Qz/Qz+Clay ratio shows its global maximum at 342 m, the Ti/Al and Zr/Al ratios are highest between 337-340 m. Furthermore, the Qz/Qz+Clay ratio strongly resembles the carbonate curve, which also supports a productivity component within the proxy.*

> We can see a long-term relationship between these proxies. However, as this time interval recorded major climatic changes, the intensity in the continental weathering considerably changed as pointed out by the osmium isotope profile generated by Cohen et al. (2004). The clay assemblage also significantly changed (see synthesis by Dera et al. 2009) explaining fluctuations in Si/Al, Ti/Al and Zr/Al. Furthermore, both Ti and Zr are supplied to the basin via heavy minerals and may explained variations in the Ti/Al and Zr/Al ratios.

*Since the sequence stratigraphic interpretation of the Sancerre core is the key issues of the paper, I would recommend a more rigorous discussion of the sequence stratigraphic model*

*and the interpretation of applied proxy data. For instance, what is meant with maximum sediment argilosity? Why does this indicate a maximum flooding? Usually this transition marks the change from retrograde to prograde sediment stacking, which means the rate of sediment supply is higher than the rate of increase in accommodation.*

> ‘Maximum sediment argilosity’ is a characteristic of periods with relatively high sea level during which the apparent clay supply is high (compared to coarse detrital mineral) as classically interpreted in boreholes from well logging using gamma-ray spectrometry and from clay mineralogy (see Pellenard et al., 1999; Coe, 2003). This is explained by maximum distance of the Sancerre site to the coast. The stacking pattern cannot easily be recognised with one section/site only, especially when dealing with core samples. The Referee is right in stating that ‘*the rate of sediment supply is higher than the rate of increase in accommodation*’, as during this key surface the relative sea level dropped. This is compatible with our attempted sequence stratigraphic framework. Nevertheless, we appreciate ‘argilosity’ is jargon and have changed this term to avoid any confusion (3.2.1.).

*Why is such a transition associated with the lowest Qz, Si/Al, Ti/Al and Zr/Al ratios in the record?*

> Maximum clay content (Al-bearing phase) explains both low quartz content, and minima in all element/Al ratios, as Al is substantially high. This is clay dilution. We have developed our explanation for this point (last paragraph of 3.3.4).

*The MRS Pl8 boundary is the most prominent surface in the core, also evident from other sections elsewhere (hiatuses at the stage boundary). The applied proxy (Qz/Qz+Clay) shows only minor changes and not a global maximum at this boundary.*

> The Pliensbachian – Toarcian boundary (and MRS Pl8) is associated with a prominent hiatus recognised at the scale of all NW European basins. The Referee spots an inconsistency with the relatively small expression of this unconformity in our Qz/Qz+Clay ratio. Indeed, the MRS Pl8 is only underlined by a ‘secondary’ spike in coarse content. As this major surface corresponds to a major hiatus, non-deposition (and possible bypass or reworking) of the sediments laid down on the seafloor may explain this relatively small mineralogical expression of this sequence boundary. The position of MRS Pl8 is resolved by the evolution in Qz/Qz+Clay and the detrital elements with a transition between an increase (regressive trend in the terminal Pliensbachian) and decrease in the ratio (transgressive trend in the earliest Toarcian). This has been explained in our new manuscript, as this point indeed required clarification. “*It may appear surprising that the stage boundary, characterised by a prominent hiatus in the European record, is only seen with a relatively small peak in the Qz / Qz+Clay curve compared to other key surfaces (Fig. 2). First, the MRS Pl8 surface is [...]*”

*How do the authors explain the fact that the highest Qz/Qz+Clay ratios are recorded during the early Toarcian transgression?*

> This is true. The highest Qz/Qz+Clay values are recorded within the Early Toarcian. This is attributable to a very modest water depth and vicinity of the coastline at the onset of the Toarcian Stage. That Qz/Qz+Clay increased within second-order T6 is explained by the **third-order** relative sea level change (transgressive system tracts of P18 and Toa1 cycles). Our Qz/Qz+Clay tool resolves depositional setting at the third order. This does not put into question the overall second-order order transgressive trend (Liassic transgression).

*Although I agree that a sufficient water depth is needed to establish shelf-sea anoxia, the authors should not forget to discuss this in the context of shelfal circulation, nutrient supply, productivity and climate change. Finally, many aspects of this study are already discussed in detail in the work of McArthur et al. (2008). The authors should spent more efforts to make it clear what are the new scientific results of their study.*

> As Sancerre was in a proximal environment, it can be assumed that nutrient supply is constantly high, and N, P and micronutrients were never in limiting concentrations for phytoplankton. The same remark may apply for DIC levels in the Jurassic high-CO<sub>2</sub> world. This point has been incorporated in the text with reference to the work by Elisabetta Erba. It is likely that %TOC fluctuated due to change in redox state of the water column rather than productivity changes. Our aim is to provide a mechanistic understanding of these ‘basinal restrictions’. Besides the production of an unprecedented sequence stratigraphic framework at this timescale for the Toarcian in the NW European, our study underlines the primary role of the relative sea level, which was not demonstrated in the insightful study by McArthur et al. (2008). We have now added this point in the conclusions to highlight the significance of our paper as suggested by the Referee (last paragraph in conclusions).

Additional references cited in the revised manuscript:

Carter, E.S., Goričan, Š., Guex, J., O’Dogherty, L., De Wever, P., Dumitrica, P., Hori, R.S., Matsuoka, A., and Whalen, P. A.: Global radiolarian zonation for the Pliensbachian, Toarcian and Aalenian, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 297, 401–419, doi: 10.1016/j.palaeo.2010.08.024, 2010.

De Wever, P. and Baudin, F.: Palaeogeography of radiolarite and organic-rich deposits in Mesozoic Tethys, *Geol. Rundsch.*, 85, 310–326, 1996.

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Wignall, P.B., Newton, R.J. and Little, C.T.S.: The timing of paleoenvironmental change and cause-and-effect relationships during the early Jurassic mass extinction in Europe, *Am. J. Sci.*, *305*(10), 1014–1032. doi:10.2475/ajs.305.10.1014, 2005.

Woodfine, R.G., Jenkyns, H.C., Sarti, M., Baroncini, F. and Violante, C.: The response of two Tethyan carbonate platforms to the early Toarcian (Jurassic) oceanic anoxic event: environmental change and differential subsidence, *Sedimentology*, *55*, 1011–1028, 2008.