Record of Early Toarcian carbon cycle perturbations in a nearshore environment: The Bascharage section (Easternmost Paris Basin)

[*submitted to Solid Earth*]

By

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RESPONSES TO REFEREE #2

Referee's comments are in black

Our responses are in blue and preceded by the sign >

The present paper, Record of early Toarcian carbon cycle perturbations in a nearshore environment: the Bascharage section (easternmost Paris Basin), by M. Hermoso and colleagues, present a new dataset (d13C, d18O, Rock-Eval data) for a section span- ning the late Pliensbachian –Early Toarcian. The authors explore whether the events recorded in the section are of local and global nature. To do so, they use carbon and oxygen isotopes, together with Rock-Eval data, and compare them to other early Toarcian sections from the similar area. They conclude that the section records the early Toarican anoxic event expressed as a positive increase of d13C values and also local events expressed by a negative CIE within the serpentinum zone. The authors discard a diagenetical issue and interpret this second event as a potential upwelling of cold deep waters 12C rich. This is one of the weak point of the current paper.

> Throughout the manuscript, we are careful on the primary record of the base of the section, and in particular, during CIE 1. Facies contain low carbonate content, which is not dominated by well preserved primary carbonate particles, such as coccoliths or calcareous dinoflagellates. This is a contrasting observation with the overlying black shales (from 4 m) and throughout the CIE 2. Indeed, during the CIE 2, the carbonate phase predominantly consists of well-preserved coccoliths, as illustrated by Figure 3 and, as referred to the work by Hermoso (2007) and Minoletti et al. (2009). Hence we rule out a diagenetic artefact on the basis of this micropalaeontological observation and that nannofloral assemblages are similar prior to (yet in black shales), during and after the CIE 2. The very good preservational state of calcareous nannofossils is a common feature of black shales nannofacies in the Paris basin and surrounding marine areas (see Röhl et al., 2001; Hermoso et al., 2009).

The authors state, and they're correct, that further data could help understanding what's happening, and they name d13C and d15N of organic matter. However, they state in the Methods section that they tried to measure OM carbon isotopic composition and failed. Why do they think they could do better in the future, and in this case why don't they wait until they have a whole dataset to publish one complete paper on this section? This is of importance in 5.3.2 where the authors use the possible changes of d13C in organic matter to support their interpretation (p. 1087 L. 12).

> We are sure that the Reviewer can understand the constraints of research in terms of logistics, financial support that may limit the immense analytical possibilities in studying a section. We felt that we had sufficiently new and self-standing data to warrant submission, as pointed out by the Referee#1. We fully agree that it would have been very useful to have $\delta^{13}C_{org}$ data. Importantly, we feel that our paper is not biased by the lack of the data. We hope that this paper will stimulate further analyses on this section to generate $\delta^{13}C_{org}$, $\delta^{15}N_{org}$, biomarkers, and perhaps TEX_{86}, given the very low thermal maturity f the organic matter. Samples are available on request to the corresponding author.

p. 1087, L12: We have removed "and organic matter" to avoid any confusion.

In the discussion, the authors state that the first (and global) CIE can be due to increased pCO2 that would be responsible for the dilution of the carbonate phase by increase detrital imputs. But increased pCO2 could increase weathering, but not necessarily erosion and detritic supply. Is the nature of the clays compatible with this suggestion? The authors additionally mention that increased pCO2 could generate lower preservation of the carbonate. They however mention that the preservation of coccolith (during the second CIE) is as good as in the rest of the section. Is this compatible with bad preservation during the first CIE? It also feels as if increased weathering and acidicifation are not necessarily compatible.

> This is true. We much welcome this comment. We have no mineralogical evidence for higher detrital supply. Again, analysing clay assemblages would be good. As we understand the Referee's statement, enhanced weathering would have led to increased alkalinity, which in turn, would have helped buffering excess CO_2 infusion from the Atmosphere to the mixed-layer. Hence, we welcome the comment, and have modified the text accordingly.

The paper reads fairly well but could be re-written in a much sharper fashion that would greatly help the reader (see detailed comments for some suggestions). The authors need to find a clear and straightforward terminology for the various CIEs/positive trends they mention, and stick to it. Figure 4 and 5 mention CIE 1 and 2, and this terminology is not used in the main text before 5.3.2. They should use "CIE 1" and "CIE 2" throughout the text.

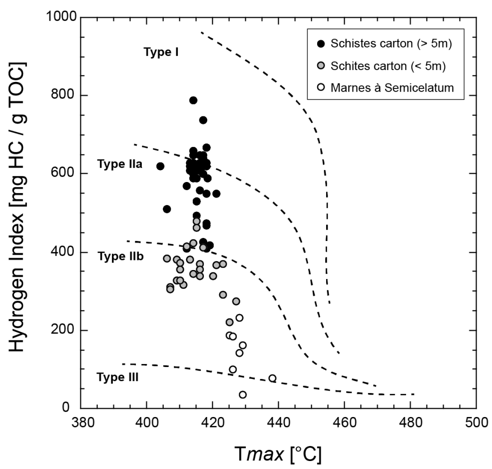
> The use of CIE 1 and CI2 is now consistently applied throughout the manuscript.

The figures are fine (axis and captions could be bigger depending on the final size of the figures), a bit repetitive however. They could add some of the environmental change on Fig. 4 and change Fig. 6 (and maybe Fig. 5) to a crossplot instead of a stratigraphic section.

> A cross-plot showing $\delta^{13}C/\delta^{18}O$ correlation will replace our old Fig. 6 (see response to Referee#1). The size of the axis label will be increased where necessary.

That would be more convincing and easier to read. A (modified) van Krevelen diagram could help instead of Fig. 5. In this regard, where does the %TOC-free come from (Methods) and is there an associated reference? Does is make sense only if the sedimentation is carbonate dominated or does it work also when the sedimention is siliciclastic or OM dominated? I would assume the sedimentaiion here is siliciclastic dominated, wouldn't it make more sense to calculate a %TOCsiliclastic- free?

> Indeed, a pseudo-Van Krevelen plot is appropriate, and more informative than the current Fig. 5 that presented HIs and T_{max} in a stratigraphic order. We will replace it by such a T_{max} / HI scatter plot (see below). An "stratigraphic" evolution in the nature of the organic matter across the subsequent lithostratigraphic units is apparent on the graph, with a progressive transition with terrestrial- to marine-dominated organic matter (Type III towards Type II).



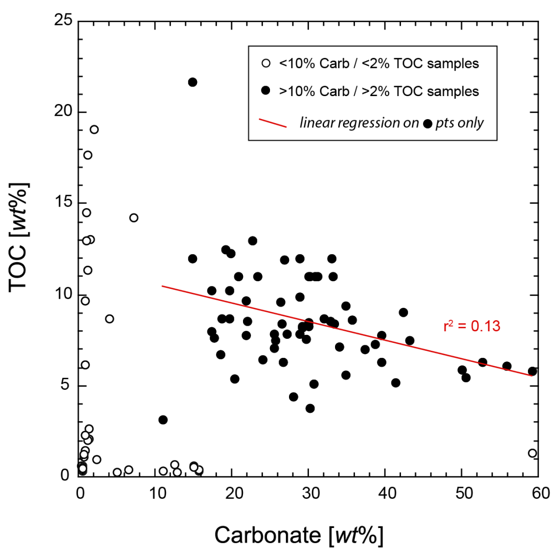
[Updated Figure (*Fig. 5)*]

TOC$_{carb\text{-}free}$ is routinely used. But we acknowledge the criticism made the Referee. It is not really an unambiguous index. Therefore, we have removed mentions of it from the text and figures. This change does not alter the substance of our discussion of the evolution of TOC in the section.

It is true that siliciclastic component would be more appropriate to discuss a dilution effect of the organic matter. However, we cannot quantify a %*wt.* Siliclastic (i.e. quartz + clay) component in the samples. An alternative method (as used by Röhl et al., 2001) would be to quantify all other main phases and assume the difference from 100% is detrital. This would require precise quantification of sulphur in sediments. Unfortunately, we do not have this data.

Actually, it would be interesting to plot %TOC vs. %carb (Ricken 1993).

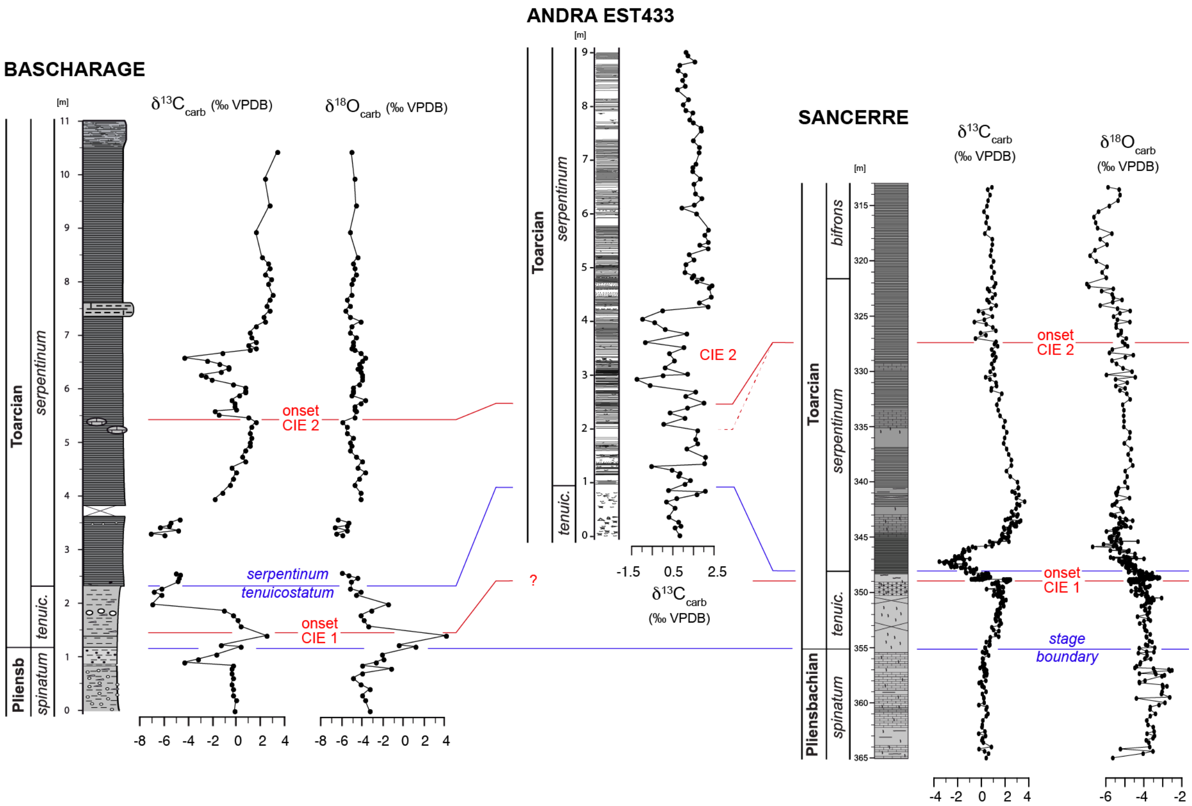
> The graph is shown below. The regression on all data is inconclusive ($r^2 = 0.03$). By disregarding very low carbonate and TOC contents (see legend iset), the linear regression coefficient is higher (0.13), but still statistically not significant. In addition, we are not able to identify "clusters" of samples that correspond to specific isotopic compositions.



Therefore, we feel that adding this figure is not really justified. We would be happy to integrate it if the Handling Editor or the Referee would like us to do so.

In 5.3.2, a figure to show the attempted correlation with the Hermoso and Pellenard would be useful. Same for the reference to the Lézin study. These claims need better support in the present paper, otherwise, these two references are not informative.

> Such a figure would be more explicit than our text. We have now attempted this correlation based on a combination of biostratigraphic and chemostratigraphic markers (blue and red lines, respectively). This figure represents a valuable addition to our work, and will be included in our revisions. The possibility of two CIEs in coeval sections of the Paris basin will be discussed in greater details in our revisions.



[*Additional Figure (Fig.7)]*. Data from Sancerre are from Hermoso et al. (2014). Data from EST433 borehole are from Lézin et al. (2013). Sancerre (Southern Paris Basin) corresponds to a much more expended section.

The authors should add the data as (supplementary) tables – or make them available to the reader.

> We agree. This will be done along with the submission of a revised manuscript.

Detailed comments

p.1074 Abstract L. 2" of the worldwide"

> "The" has been added.

L.9: state that Bascharage is in the Lux. Sed. Area. I'm not sure you need to mention the "so-called Gutland.

> "Gutland" has been removed.

L.15: define T-CIE

> Toarcian CIE (T-CIE).

L.19 "expressed as four negative steps"

> Corrected.

p. 1075 the end of the abstract (l.1-4) is not useful, and not supported by the paper. I don't think integrated approach is a new idea.

> This sentence is deleted.

Introduction l. 14 untangle, not detangle

> Change made.

l.20 minor portion, instead of tiny portion?

> "Minor" now replaces "tiny"

l.21 "are recognized based on..."

> Done.

l.24-25: "with substantial organic carbon content" instead of "accumulation of OC" would make more sense, except it sedimentation rates are known.

> This is true. The sentence has been changed accordingly.

p. 1076 l.10 "in addition" instead of "If this was not complicated enough"

> Done.

l.11 Remove "more broadly speaking"

> Done.

l.18 Remove somehow

> Removed.

l.20 eastern instead of oriental

> Done.

l.27 "we characterize" or "we describe" instead of "we attempt"

> We go for "characterise".

The Bascharage composite section p.1077 l.13: composed of

> "of" replaced "by"

l.14: what does "temporally exposed" mean?

> We meant to say that the section is not accessible anymore. We have removed the word "temporally". The past tense of the sentence is explicit.

l.17: I'm not familiar with the notion of "conservative non-observational hiatus". Maybe this could be explained further.

> "conservative" has been changed for "maximum"

Methods p.1079 l.9 How is reproducibility defined?

> This is an internal reproducibility from repeated measurements of an in-house standard. This information has been added.

Results p.1080 l.20 "deposits are characterized by low to extremely low carbonate content"

> OK

p.1081 l.1 remove "comprised"

> Done.

l.3 remove "that is"

> Done.

l.20 rocks instead of rock

> Done.

L.21 Revert both sentences: :During the Pl., ratios are stable... The d13C values are strikingly negative. . ." Otherwise, this would mean that the first CIE is not reliable.

> This changes has been made.

p. 1082 l.2 "When a carb. fraction reappears" is a strange sentence.

> "With carbonate content increasing from 3.4 m…"

l.20 are not as intense as

> "as" replaces "so"

l.26 performed instead of attempted.

> Change made.

l.26: your statement is confusing. In the methods, you say that TOC were determined with a Rock-Eval machine. So, the Rock-Eval data are collected for all samples. Maybe you should write instead "We used the Rock-Eval characterization of the OM only for TOC content above ~1%"

> Indeed! Change made.

l.27 Below instead of in advance

> Done.

Discussion p.1083 Here, you state that the OM is continental. Rock-Eval alone is not enough to be fully sure. Later (p.1085), you mention that you recovered wood fragments. Why not use this piece of information here instead of in paragraph 5.2? Did you observe these fragments, are they documented, or is it an observation from the literature?

> We observed wood (sometimes bark) fragments at this level, as indicated in the Fig. 2. We mention this in part 5.1. in the revised manuscript. As it is now shown on the new Fig. 5, relatively low Hydrogen Index are indicative of a continental-derived organic matter. This true that occurrence of wood provides supplementary evidence for this. However, this level belongs to the Lower Toarcian Schistes carton lithostratigraphic unit, and therefore is well placed in 5.2., rather than in 5.1., which is dedicated to the Stage boundary.

p.1084 l.1 to 5: You can remove this part. There is no point in saying what the signal is not (or add references. Even if they are well-known interpretations, they still can use a reference).

> Sentence deleted.

l.9 orange clays instead of orange clayed?

> Changed.

L.20 the d13C values suddenly drop instead of "this composition. . .dropping"

> Done.

L.22 remove "in this stratigraphic level"

> Done.

L.22 "with the well-documented early Toarcian negative CIE (CIE 1 in Fig. 4) " add references. I'm sure there are other studies than Rohl and Hermoso.

> References added: Hesselbo et al. (2000); Kemp et al. (2005); Caruthers et al. (2011); Gröcke et al. (2011); French et al. (2014).

p.1085 l.23: the second CIE is within the serpentinum zone.

> This has been changed.

l.25: add ref. about this positive trend.

> We now refer to the review by Jenkyns (2010)

l.26: add ref. about the Med. sections.

> Hesselbo et al. 2007; Woodfine et al. (2008); Sandoval et al. (2012)

p.1086 paragraph 5.3.1 is a bit misleading, suggesting that the present study contains new data about the preservation state of the calcareous nannofossils. Fig. 3 comes from Minoletti et al., 2009 (as clearly stated in the caption), this should be made clear in the text as well.

> This is true. These observations have been originally made by Hermoso (2007) and Minoletti et al. (2009). This point will be more clearly stated in our revised manuscript ("examination of nannofacies by Hermoso (2007) and Minoletti et al. (2009) …)

p.1087 L.7: "during the second negative CIE” instead of "during the negative CIE"

> Done.

L. 9: remove firstly

> Done.

L.11: remove (organic)

> Done.