

## ***Interactive comment on “An open marine record of the Toarcian oceanic anoxic event” by D. R. Gröcke et al.***

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This manuscript presents and discusses an organic carbon isotope record across the early Toarcian interval from a section in Japan. A series of interesting and related suggestions emerge from the presentation and discussion: (1) a prominent negative carbon isotope excursion can be found at this location, (2) the minimum value is -57 per mil; (3) a drop in dissolved O<sub>2</sub> occurred at approximately the same time (though see below); (4) the carbon isotope excursion signifies a rapid and massive input of <sup>13</sup>C-depleted carbon to the ocean and atmosphere; (5) the carbon isotope excursion and the drop in dissolved O<sub>2</sub> (though see below) were caused by release and oxidation of methane.

It is worth pointing out that I am not an expert on the Early Toarcian. As such, I cannot

C95

comment on certain aspects of the manuscript (e.g., stratigraphic details, completeness of referencing, etc.).

Nonetheless, if some to all of the above points can be bolstered, this strikes me as a very nice contribution. Unfortunately, there are some problems with the present work. These involve incompletely framed ideas and missing data. As such, I would recommend publication only after major revisions, and inclusion of some additional data.

I trust that this review is fair and constructive.

Sincerely,

Gerald Dickens

Main Comments

(1) Comparisons between the early Toarcian and the early Paleogene are inescapable because similar sets of records seem to span both intervals. This is important because many of the arguments and discussions regarding the extent, magnitude, timing and cause of the negative carbon isotope excursions are similar. Even the progressions of arguments and discussions have been similar, with those for the PETM offset by about one quinquennium.

This is noted at the end, but I also would state this at the beginning (Page 387, Line 18). Some of the discussions regarding the early Toarcian over the last five years have been framed without recognition that at least one rapid and massive input of <sup>13</sup>C-depleted carbon to the ocean and atmosphere almost assuredly occurred at about 56 Ma.

(2) The discussion of intermediate water O<sub>2</sub>-deficiency (Page 393, Lines 15-28; Page 394, Lines 1-3) needs rethinking and rewriting.

First, some of this discussion is confusing.

More importantly, the idea of intensified O<sub>2</sub> deficiency beneath the Equator because of

C96

enhanced surface productivity is not correct as written. The dissolved O<sub>2</sub> concentration of a parcel of water beneath the mixed layer depends on the integrated consumption of organic carbon along the flow path. So, in the modern Pacific Ocean, the dissolved O<sub>2</sub> concentration of intermediate water does drop near the Equator; however, it continues to drop to the north because dissolved O<sub>2</sub> is not being added to the water as it moves away from the Equator. Consequently, dissolved O<sub>2</sub> concentrations are actually lower beneath the north Pacific gyre, which has low surface water productivity, than beneath the Equator, which has relatively high surface water productivity. I suspect this interesting concept applies throughout the Phanerozoic, although the effect should depend on the direction and age of deep-water flow. With water flow similar to present-day, a site at intermediate water depths in the central Pacific would not traverse through higher dissolved oxygen conditions as it moved north from the Equator.

(3) The stratigraphic link between changes in carbon isotopes and changes in dissolved O<sub>2</sub> can and should be improved. It should also be presented and discussed more thoroughly. See, for example, the paper by Nicolo et al. concerning the PETM (Paleoceanography, 2010).

(4) The discussion of sedimentation rates and primary productivity also needs rethinking and rewriting. The stated (compacted) sedimentation rate for the interval of interest is 1 m/Myr (Line 391). This is very slow deposition, especially given the suggestion that there was elevated primary productivity. For example, Plio/Pleistocene sedimentation rates at open-ocean sites of the Pacific within a few degrees of latitude of the Equator are on the order of 20m/Myr.

(5) The correlation between d<sup>13</sup>C records (Figure 3) is interesting but not very compelling for three reasons. First, the ties between various radiolarian and ammonite zones are not crystal clear. Second, the resolution of the Katsuyama carbon isotope record is too low for such correlation; most of the d<sup>13</sup>C tie points are defined by a single high or low value, in contrast to the other records. Third, the most prominent low must be explained by a difference in the composition of organic carbon (below),

C97

but this necessarily means that some portion of the record is not reflecting variations in the exogenic carbon cycle, which is the basis for such correlation in the first place. The resolution of the record should be enhanced; otherwise, the primary arguments and suggestions in the manuscript cannot be defended rigorously.

(6) The sample with the unusually low d<sup>13</sup>C value is very intriguing and potentially very important. Most methane escaping from modern seeps on continental slopes (including man-made ones courtesy of BP) is oxidized in the water column by microbes. Consequently, various people have looked for evidence of methanotrophy (exceptionally low d<sup>13</sup>C in organic carbon, biomarkers, or both) across PETM sequences; nothing has been found to date. There are at least three possible explanations for this: the d<sup>13</sup>C excursion across the PETM has nothing to do with seafloor methane release and water column methane consumption; molecular evidence for water column methanotrophy is not preserved in ancient marine sediment; the sites which would contain this evidence across the PETM have not been examined. The latter is certainly possible for the PETM, because we have very few if any PETM sections from appropriate locations (i.e., from continental slope settings or the deep North Atlantic where methane seepage might have occurred). So, this raises a curious question: why would we find such evidence in Early Toarcian sediment deposited on a seamount in the central Pacific Ocean? It also raises two direct and immediate questions: is this low d<sup>13</sup>C value reproducible? What does it actually signify? The sample should be re-examined for its carbon isotope composition and examined for its molecular chemistry.

Other comments (admittedly some very pedantic):

– Page 387 – Lines 10-11: This probably should read "... postulated to represent a decrease in the <sup>13</sup>C/<sup>12</sup>C ratio of the entire global carbon cycle, caused by a massive input of <sup>13</sup>C-depleted carbon (REF)."

Lines 21-23: This sentence is awkward to read.

– Page 388 – Line 4: Change shelf to slope. Gas hydrates cannot occur on most

C98

shelves because of phase boundary considerations (insufficient pressure).

– Page 389 – Lines 13-15: I do not follow this. How were the sediments deposited on seamounts and in trenches?

– Page 390 – Line 5: These were not drilled by the IODP but by the ODP.

Lines 12-15: I do not follow this. How do the polarity chrons record latitude? I am assuming there is something about magnetic inclination in the data.

– Page 391 – Line 1: Does the 200 cm refer to the dimensions or stratigraphic position of the MnCO<sub>3</sub> spherules? I am assuming the latter if indeed cm, but they are not shown on the log (Figure 2), and it would be interesting to know their size.

– Page 392 – Lines 25-26: Clarify this. What does “Costech was set to Macro-O<sub>2</sub>” mean? What does “done in no dilution mode and all results produced more than 1000 m” mean?

– Page 394 – Lines 10-11: This is imprecise as written. Clearly, very low δ<sup>13</sup>C values of organic matter can be found at present-day.

– Page 398 – Line 13: Here is a quote to consider regarding this idea:

“Present-day atmospheric and combined ocean reservoirs contain  $\sim 1.2 \times 10^{21}$  g and  $\sim 6.8 \times 10^{18}$  g of O<sub>2</sub>, respectively (Walker, 1980). Thus, addition of  $1.4 \times 10^{18}$  g of CH<sub>4</sub> to the atmosphere or ocean would not significantly decrease the O<sub>2</sub> content of the atmosphere. However, because O<sub>2</sub> exchange fluxes between the deep ocean and atmosphere take on the order of  $10^{13}$  yr, if a substantial fraction of the CH<sub>4</sub> was oxidized in the ocean, there should have been a brief time interval of significant oceanwide O<sub>2</sub> depletion during the LPTM” – Dickens et al., *Geology*, 1997.

Quite simply, there is far too much O<sub>2</sub> in the atmosphere. Consumption of O<sub>2</sub> in the ocean – yes; consumption of O<sub>2</sub> in the atmosphere – no.

Line 15: Why would enhanced productivity decrease the O<sub>2</sub> concentration of the at-

C99

mosphere? This seems backwards. In any case, given the short time-scale of the event and the tremendous amount of O<sub>2</sub> in the atmosphere, I don't think it's likely that variations in productivity across the event would impact atmospheric O<sub>2</sub> very much.

Lines 27: The evidence for a massive input of <sup>13</sup>C-depleted carbon across the PETM is very compelling. However, it is certainly debatable as to whether it was a “clathrate dissociation event”. I would rewrite this.

– Page 400 – Line 3: There is good evidence for O<sub>2</sub>-deficiency across the PETM (e.g., Nicolo et al., *Paleoceanography*, 2010). However, I am unaware of any deep-water black shales across the PETM.

Figure 2: Are the red “bubbles” the MnCO<sub>3</sub> spherules mentioned in the text or nodules of red chert? This is not clear from the figure or caption.

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