

## ***Interactive comment on “Methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events: setting appropriate parameters for discussion” by G. R. Dickens***

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Dear Ellen,

Thank you very much for the thoughtful and insightful comments!

Some will be difficult to address without modifying the flow and emphasis of the present manuscript significantly. This is because they lie at the root of important issues that cannot be answered satisfactorily without extensive additional text, newly acquired data, or both. You have raised (not unexpectedly!) several wonderful discussion topics.

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I have taken liberty to number each of the paragraphs to aid discussion. For better or worse, I have tried to answer the difficult comments with engaging thought, some which might frame very good targets for future investigations.

I respond thusly:

(1) The first paragraph includes two separate items for discussion. (1a) McCarren et al. (G3, 2008) benthic foraminifera carbon isotope records from Walvis Ridge sites are interesting, in part because they suggest a -3.5 per mil or greater  $\delta^{13}\text{C}$  excursion at the shallowest location (Site 1263). This likely represents deposition at intermediate water depths.

There are, however, two overarching and perhaps related problems regarding sites from Walvis Ridge and several other locations in the central and north Atlantic: (i) this region had a much smaller water volume (nominally 50%) in the early Paleogene than at present-day because of plate motion; (ii) this region had much stronger seafloor carbonate dissolution during the PETM than in other regions.

Around 66% of the modern exogenic carbon cycle (by mass) occurs as dissolved inorganic carbon within intermediate and deep waters of the Pacific, Indian and southern Oceans (the actual amount depending on how one slices vertical and horizontal boundaries, and characterizes marine and terrestrial organic carbon pools). This “carbon mass majority” was almost assuredly even larger in the early Paleogene – about 75% or so – if one includes the now-destroyed Pacific and eastern Tethys regions. From the start of any discussion, it should be clear that records from central and north Atlantic may not represent intermediate and deep waters across the globe quantitatively.

From a modeling perspective, two generic causes have been offered for the enhanced carbonate dissolution in the central and north Atlantic during the PETM (Dickens, Bull. Geol. Soc. France, 2000; Zeebe and Zachos, Paleogeography, 2007). These are: (a) preferential input of  $^{13}\text{C}$ -depleted into deep and particularly intermediate waters of the Atlantic, and (b) a switch in deep-water sources and flow, such that less deep

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water was formed in the north Atlantic during the PETM. The concepts are not mutually exclusive.

The first of these explanations could arise because of thermogenic methane sources in the north Atlantic (e.g., Svensen et al., *Nature*, 2004; Dickens, *Nature*, 2004), or because of methane inputs from gas hydrates (Dickens, 2000). For gas hydrates, the plausible explanation lies in the relative proportion of continental slopes to total basin volume; if continental slopes served as point sources of methane during the PETM, and methane oxidation to carbon dioxide occurred fairly quickly in the water column (see below), CO<sub>2</sub> inputs could have been disproportionately greater in smaller ocean basins with higher slope area to water volume ratios (Dickens, 2000).

Either explanation for the enhanced carbonate dissolution is interesting to interpretations of carbon isotope records at Walvis Ridge, because they almost necessitate that changes in  $\delta^{13}\text{C}$  of intermediate to deep waters should be enhanced in the central and north Atlantic relative to the much larger Indo-Pacific region. In other words, the -3.5 per mil or greater  $\delta^{13}\text{C}$  excursion at Site 1263 may be telling us very important information beyond the average change in the  $\delta^{13}\text{C}$  of average ocean DIC.

The community absolutely needs Lower Paleogene records of stable isotope and carbonate dissolution from "Walvis Ridge-type" locations in the Indo-Pacific region. Without these, it is very difficult to constrain the early Paleogene carbon inputs beyond the uncertain estimates currently available.

Interestingly, if either explanation given above for the differential carbonate dissolution is correct, and if pH and dissolved O<sub>2</sub> are primary factors causing "missing" benthic foraminifera across the onset of the PETM in several Atlantic records, one might predict better and more complete benthic foraminifera records at comparable sites in the Pacific and Indian Ocean. I will go "out-on-a-limb" and suggest that these records can be recovered (e.g., possibly at Broken and Ninety-east Ridges), and that, when generated, they will show more modest carbonate dissolution and carbon isotope excursions

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than at Walvis Ridge.

(1b) Paired stable carbon isotope analyses of carbonate and organic carbon provide interesting information. However, in the cited cases of the commentary, the carbonate material analyzed is shallow to deep marine, whereas the organic carbon material analyzed is terrestrial. Moreover, while the terrestrial organic carbon material is sometimes compound-specific (e.g., a C-NN alkane), the single compound can derive from multiple sources. Consequently, for such records, various and distinct processes might impact both records through fractionation, and they precipitated from the different carbon pools. This is specifically why I raised the New Jersey carbon isotope records of single-species foraminifera and Apectodinium in the manuscript. In this case, I think unique so far, we are confronted with analyses of single phases of marine carbonate and marine organic carbon from the same shallow location, and both show a -4.5 per mil excursion across the PETM. Given the parameters of the location, it is not so easy to dismiss both records via a process that would enhance only one of the records, including especially pH.

Interestingly and importantly, pH has a significant effect on carbon isotope fractionation of marine carbonate (Uchikawa and Zeebe, 2010). I do not think the significance of this fact has been fully appreciated. It is not so simple to argue that >4 per mil excursions in carbonate and organic carbon represent a truly massive input of carbon, particularly into the atmosphere. If this was the case, one then needs to explain how and why this works, as there should be an offset between the  $\delta^{13}\text{C}$  excursions in organic carbon and marine carbonate on the New Jersey shelf or elsewhere.

It would be fantastic to see more paired records of marine carbonate and marine organic carbon across the PETM and other hyperthermals. Unless the chosen marine organic compounds are compromised by fractionation effects, I will go "out-on-another-limb" and suggest such paired records will show similar magnitude excursions, implying a relatively small decrease in the pH of surface water DIC.

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Of course, one needs to also realize that all analyses on shallow marine and terrestrial carbon are missing the lion's share of the exogenic carbon cycle, as noted above. In the end, mass balance arguments across the PETM and other short-term carbon injection events of the early Paleogene need to be set from phases recording the composition of intermediate to deep water in the Indo-Pacific region.

(2) I totally agree that the salinity effect on  $\delta^{13}\text{C}$  of DIC depends on the  $\delta^{13}\text{C}$  (and DIC concentration) of river water, and thought that I made this point (p. 1148, Lines 1-2).

Interestingly, if lowered  $\delta^{13}\text{C}$  in carbon-bearing phases across the New Jersey shelf were related to greater fresh water discharge during the PETM,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  excursions should be amplified toward the coast. So, your stated observations across the shelf make sense to me. I knew of some of these records, but was reluctant to expand on the salinity idea too much, because I did not want to detract from potential future interpretations by those who generated the data.

The fact that benthic foraminifera carbon isotope excursions across the New Jersey shelf also become magnified across the PETM is intriguing. Equally intriguing is the notion that, because of enhanced fresh water discharge, the water on this shelf became more stratified during the PETM (e.g., Lippert and Zachos, *Paleoceanography*, 2007).

I will suppose that the  $\delta^{13}\text{C}$  composition of carbon-bearing phases across this and other shelves during the PETM depend on salinity gradients and stratification, and that both effects may impact carbon isotopes of DIC. I have endeavored to go through the literature on this topic; it is surprisingly scarce.

The fact that we cannot find terrestrial organic carbon or palynomorph records to support greater riverine discharge on the New Jersey margin remains a perplexing issue, especially because other evidence (e.g.,  $\delta^{18}\text{O}$  of planktic foraminifera, sedimentation rates, redox conditions) suggests that it did increase significantly.

It would be very interesting to see gradients of the  $\delta^{13}\text{C}$  of DIC (with coupled salinity)

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across modern margins in the vertical dimension and also in 3-D. How exactly does riverine discharge affect the  $\delta^{13}\text{C}$  of DIC throughout the water column across various shelves?

There are also remarkably few published records showing both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of single-species foraminifera (and other phases) across shelves beyond New Jersey during the PETM and other hyperthermals. Can  $>4$  per mil changes in the  $\delta^{13}\text{C}$  of planktic and benthic foraminifera be documented across shelves and during the PETM where the  $\delta^{18}\text{O}$  and other indications do not support enhanced riverine discharge? I will predict no.

(3) Clearly, I need to reword part of this paragraph, given comments by you, Matt and other colleagues sent by direct email. I have no issue with some fraction of carbon, including as methane, entering the atmosphere directly. However, it makes no sense to argue that ALL methane released from gas hydrate dissociation would enter the atmosphere and drive ALL the temperature rise during the PETM and other hyperthermals. Otherwise, how would widespread gas hydrate dissociation occur in the first place? Some component of deep ocean temperature rise must happen first for this explanation to be valid.

I think the following is an appropriate and accurate modification of the last sentence "There was never a suggestion in original papers that all  $\text{CH}_4$  inputs from the seafloor entered the atmosphere and drove all climate change during the PETM."

The bit on methane release, bubble formation and the proportion of potential methane consumption warrants further commentary.

First, the rise of methane bubbles above seeps in the Gulf of Mexico may be atypical because the bubbles can be coated with oil (MacDonald et al., *Geofluids*, 2002). This probably does not happen at most locations; instead, bubbles become coated with gas hydrate and rise to the depth where the hydrotherm crosses the gas hydrate stability zone (e.g., Paull et al., *Geology*, 1995; Heeschen et al., *GRL*, 2003).

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Second, as emphasized in Dickens et al. (Paleoceanography, 1995) and in all subsequent works with me as a co-author, if methane release from gas hydrates is the correct explanation for early Paleogene carbon isotope excursions, such carbon input must come from continental slopes at 900+ m water depth. This comes straight from the dual notions of warmer bottom waters in the early Paleogene (Zachos et al., Science, 2001; Nature, 2008), and from the phase boundary conditions for methane hydrate in seawater (Dickens and Quinby-Hunt, GRL, 1994). There is very little play here. Indeed, this hits at the problem discussed in the last part of the manuscript – the global gas hydrate stability zone along continental slopes must have been smaller in the early Paleogene than at present-day, because the top and bottom would have been “shaved off” with warmer bottom water (Dickens, Organic Geochem., 2001). Here, however, it is absolutely crucial to emphasize that this is the potential volume of pore space where gas hydrate can occur, not the mass of methane stored within this pore space, which depends on the inputs and outputs of methane.

Note also that the aforementioned crossover depth would have been at ~900 m during much of the early Paleogene, rather than ~450 m in much of the present-day ocean (again from phase boundary considerations, Dickens and Quinby-Hunt, 1994).

Third, it appears that much of methane released during the recent Deep-Horizon debacle was consumed within the water column (Kessler et al., Science, 2011; Joye et al., Nature Geoscience, 2011).

In summary, if large amounts of methane were released from the seafloor during the PETM and other hyperthermal events, a significant fraction would probably have been oxidized within the water column.

In any case, I am perplexed by the last sentence. We have tried, admittedly crudely, to model the amount of oxygen deficiency that could be caused by methane release into intermediate and deep-ocean waters during the PETM (Dickens, 2000; Nicolo et al., Paleoceanography, 2010). The answer, of course, depends on several key factors,

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including the timing and mass of potential methane input. Nonetheless, with “modest” rates and masses for postulated methane inputs (>10,000 years; <3000 Gt), and especially considering the probable location – intermediate water depths – the whole ocean does not go anoxic!

With a large methane input from continental slopes, I would expect widespread O<sub>2</sub>-deficiency, especially at intermediate water depths where methane was released, but not anoxia everywhere. Moreover, if the idea of massive seafloor methane release is correct, I would predict that, at intermediate water depths, such O<sub>2</sub>-deficiency should correspond to the carbon input. This is precisely why we chased and quantified the bioturbation records at the Mead Stream section, which demonstrate these predictions (Nicolo et al., 2010).

Given our interpretations for the Mead Stream section, and the aforementioned ideas regarding carbon inputs across the PETM (Comment 1, above), the idea of methane driven O<sub>2</sub>-deficiency can (and should) be assessed with records at other sites and much better numerical modeling. For example, sites that accumulated sediment at intermediate water depths, especially in the north and central Atlantic (e.g., some at Demerara Rise), should show O<sub>2</sub>-deficiency coincident with that of carbon input at the start of the PETM.

(4) Agree, and will include.

(5) Agree, and will include.

(6) There are some unfortunate coding errors in the Walker and Kasting (1992) model that I did not realize and appreciate until 1999. (nb. the Dickens, Bull. Geol. Soc. France, 2000 paper was actually written and accepted in 1998). The basic problem in a nutshell is that, given a mass and composition of some <sup>13</sup>C-depleted carbon input, the δ<sup>13</sup>C response is too large while the carbonate dissolution is too small. Carozza et al. (GRL, 2011) have discussed this problem and modified the model accordingly.

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I have never been overly bothered about this problem, once recognized, because the basic arguments and discussion in Dickens et al. (1997) and Dickens (2000) remain correct semi-quantitatively, and because a semi-quantitative perspective was the stated premise in these papers, given that masses for present-day carbon cycle reservoirs are almost assuredly different than those of the early Paleogene.

So, yes, in Dickens et al. (1997) and Dickens (2000), the carbonate dissolution is probably too small for the given carbon input. Nonetheless, we are confronted with the basic problem that seafloor carbonate dissolution (as well as O<sub>2</sub> deficiency) appears much greater in the north and central Atlantic than in the much larger Indo-Pacific region. This is a fundamental and absolutely important observation if correct, irrespective of the quantitative details (Dickens, 2000; Zeebe and Zachos, 1997; Panchuk et al., *Geology*, 2008; Zeebe et al., *Nature Geoscience*, 2009).

A truly outstanding problem is that there are remarkably few records in which to constrain the CCD before the PETM, especially in Indo-Pacific basins, which sets the baseline for how carbonate dissolution responds to massive carbon input. We have specifically targeted the sequences at Sites 259 (Hancock et al., *Int. J. Earth Sci.*, 2007) and 1215 (Leon-Rodriguez, P3, 2010). Available records suggest that the CCD deepened from about 57 to 50 Ma, and hence the offhand notion that this might be driven by AOM rather than weathering.

We do know, from a few sites, including through recent drilling (IODP Expedition 329), that the CCD was never really deep in the early Paleogene, and it never over-compensated after a carbon injection by a large amount during this time. Both observations suggest that the carbon input, while large, was not huge.

(9) Yes, I should include reference to Stap et al. I also know that several abstracts have discussed the general idea of “photosymbiont ejection” during the hyperthermals, but have yet to see a paper on this topic. This would be nice to see.

(10) I have to admit that I am confused by this comment on past benthic foraminifera

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distributions, so I am uncertain how I might address it into the manuscript or the discussion. The key factor for gas hydrate systems is the time integrated supply of organic carbon to the slope. Right now – the Holocene – is not a good time to understand and frame such deposition, because it contrasts markedly with average conditions over the last million years. Does the shelf-slope distribution in the Paleogene look more like interglacial or glacials? In any case, I am not so sure the link between foram distributions and organic carbon accumulation in slope environments can aid in this important concept without selecting ideal sites.

(11-13) Agree, and will include.

Jerry

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Interactive comment on *Clim. Past Discuss.*, 7, 1139, 2011.

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