

## ***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 Sabine,

As always with your reviews, some excellent comments that force some rewriting and rethinking.

1/ I partly agree with the comment regarding bicarbonate production and carbon isotopes in gas hydrate systems. I will add a paragraph to clarify things.

I elaborate below in detail for any and all interested readers, because this comment  
C870

raises an absolutely fundamental issue. I should also note that we have a paper arriving shortly that provides backbone on this topic from the perspective of modeling pore water profiles above modern gas hydrate systems (Chatterjee et al., JGR, in press).

The placement of a large, dynamic seafloor methane cycle (or for that matter any similar such  $^{13}\text{C}$ -depleted reservoir) into the global carbon cycle needs to account for both production of  $^{13}\text{C}$ -depleted methane and production of  $^{13}\text{C}$ -enriched bicarbonate. Basically, one cannot invoke conversion of organic carbon ( $\delta^{13}\text{C}$  of -25 to -30 per mil) to methane ( $\delta^{13}\text{C}$  -60 to -70 per mil) and store this methane without accounting for the fate of the  $^{13}\text{C}$ -enriched carbon.

We know that, during methanogenesis, both  $^{13}\text{C}$ -depleted methane and  $^{13}\text{C}$ -enriched bicarbonate form. One only needs to look at the profiles of alkalinity and the  $\delta^{13}\text{C}$  of DIC in most boreholes where gas hydrate has been drilled (e.g., Legs 164, 201 and 204 of the Ocean Drilling Program). Alkalinity and the  $\delta^{13}\text{C}$  of DIC are typically very high (ALK 50-200 mM;  $\delta^{13}\text{C}$  of DIC +5 to +20 per mil).

In the Dickens (EPSL, 2003) paper, I suggested that the  $^{13}\text{C}$ -enriched bicarbonate ultimately precipitated as authigenic carbonate within the zone of methanogenesis (i.e., deep in the sediment and well below the sulfate-methane transition, SMT). This was for two reasons: (a)  $^{13}\text{C}$ -enriched carbonate (as siderite and dolomite) has been documented in deep sediment at several locations with gas hydrate (e.g., Blake Ridge, Rodriguez et al., ODP Proc. Sci. Res. 164, 2000); (b) I did not fully appreciate the “open nature” of gas hydrate systems. Basically, I needed to remove the  $^{13}\text{C}$ -enriched bicarbonate from a modeling perspective, so it was easiest to bury it away (ha ha!).

This view is incorrect, as noted in your comment (and which I thought I stated in the submission). Far more crucially, it overlooks, in my opinion, a very important concept: most of the  $^{13}\text{C}$ -enriched bicarbonate formed during methanogenesis returns to the ocean. This is true for some systems with venting, as stated in your comment, but I think this is true for many gas hydrate systems (e.g., Blake Ridge, Peru Margin, Hy-

drate Ridge, etc). The keys to realizing this are seven-fold: (a) pore water alkalinity gradients always increase steeply between the seafloor and the SMT; (b) the slopes of these gradients, even after including downward sediment burial, necessarily imply an upward flux of DIC from the SMT to the seafloor; (c) pore water alkalinity gradients often (though not always) continue to rise below the SMT, but at a slower rate, suggesting an upward input of DIC from depth into the SMT; (d) this means that, in many locations, there is an inflection in alkalinity (and DIC) at the SMT, which is probably caused by inputs from two sources, AOM and upward rising DIC; (e) pore water Ca profiles consistently show “concave-down” inflections across the SMT, suggesting authigenic carbonate precipitation at or near the SMT, but flux calculations always show that much less carbon leaves the SMT as carbonate than enters the SMT as bicarbonate (through AOM and deeper sources); (f) the  $\delta^{13}\text{C}$  of DIC at SMT is always depleted in  $^{13}\text{C}$  relative to seawater but generally enriched in  $^{13}\text{C}$  relative to that methane (i.e.,  $\delta^{13}\text{C}$  of DIC -60 to -10 per mil). (g) across numerous sites where gas hydrate occurs in underlying sediment, there is a first order correlation between the alkalinity concentration at the SMT (from 15 to 60 mM), the sum total of carbon fluxes into the SMT, and the  $\delta^{13}\text{C}$  of DIC at the SMT (from -60 to -10 per mil) (see Chatterjee et al., JGR, in press).

Thus, I fully agree that most of the bicarbonate entering the SMT (via AOM AND THE DEEP FLUX of  $^{13}\text{C}$ -depleted bicarbonate) does not precipitate as carbonate in shallow sediment. Luff and Wallman (GCA, 2003) were the first to point this out; others working in completely different systems have also realized this (e.g., Snyder et al., DSR, 2007).

Point (g) is the really cool observation. I do NOT think this is because AOM is relatively unimportant at many of these sites, as argued in many papers, despite evidence to the contrary. Instead, it is because the upward fluxes of methanogenesis products (methane and bicarbonate) are mixing at the SMT in different proportions.

There is no doubt in my mind that circa 2011: (a) large amounts of  $^{13}\text{C}$ -enriched bicarbonate (as alkalinity) form during methanogenesis in gas hydrate systems; (b) this

C872

bicarbonate escapes to the ocean along with methane at present-day (and presumably through time); and, (c) the fluxes of these two “return” carbon inputs (methane and bicarbonate) are significant but can vary at the local and global scale.

This view has at least two interesting ramifications.

First, one cannot examine the  $\delta^{13}\text{C}$  of DIC in pore water or the  $\delta^{13}\text{C}$  of authigenic carbonate formed above methane systems and distinguish between processes of organic carbon consumption. For example, one might find DIC or carbonate proximally caused by AOM at the SMT with a  $\delta^{13}\text{C}$  of -10 per mil, but in a system where the upward flux of  $^{13}\text{C}$ -enriched bicarbonate is greater than the upward flux of  $^{13}\text{C}$ -depleted methane (in principle, because among other reasons, the methane is being stored into gas hydrate).

Far more crucially, it impacts interpretations of ocean  $\delta^{13}\text{C}$ . In the Dickens (EPSL, 2003) paper, I indicated that long-term positive and long-term negative excursions could not be driven with a methane capacitor, but this was, to a large part, because my model did not have  $^{13}\text{C}$ -enriched carbon formed during methanogenesis returning to the ocean. Once this framework is broken, then, wow, at least theoretically, long-term  $\delta^{13}\text{C}$  excursions, positive and negative, can be driven through slow methane storage and release.

Ultimately, your comment highlights a wonderful “bottleneck” that has consumed my thoughts and efforts for several years. I think small but significant amounts of  $^{13}\text{C}$ -depleted bicarbonate are leaking out of gas hydrate systems, everywhere, right now. The composition of this bicarbonate depends on the relative fluxes of methane and deep bicarbonate formed by methanogenesis. That is, there are inputs and outputs of carbon from the seafloor as depicted in the figure of the paper, although the fluxes at present-day, let alone the past, are highly debatable. (A great constraint lies in  $^{14}\text{C}$  budgets, but I am unaware of anyone who has incorporated and tested this notion; maybe this response will prompt someone . . . or I will eventually get to this tick mark

C873

on things to do). I am stuck, however, because many marine geochemistry colleagues either do not agree with this idea or have not yet “hopped on board”.

I would like to move past this issue, because when one looks at the sum total of data for modern gas hydrate systems, the arguments in support of the above comments are very compelling, at least in my opinion (and hence the forthcoming Chatterjee et al. paper in JGR). However, this is a “deal-breaker”. If both products of methanogenesis (13C-depleted methane and 13C-enriched bicarbonate) are not returning to the seafloor at present day, the entire idea of a large and dynamic gas hydrate capacitor during the early Paleogene (and other time intervals) probably falls apart. So, definitely correct me if I am wrong.

2/ Yes, I see the confusion in the writing. In this case, it would be methane outputs through AOM not through aerobic oxidation in the water column. I will rewrite.

On this note, I should probably stress more clearly and emphatically that there are two fluxes of methane from the seafloor at present-day (and presumably in the past) – AOM in shallow sediment, and aerobic oxidation of methane in the water column – and both can vary independently in the time domain. I tried to do this in the figure, but I find it a difficult concept to convey simply.

3/ The sedimentary record of authigenic mineralization (and biomarkers for methanogenesis and methanotrophy) is the “Achilles Heel” to the overall idea. Since very few (if any) people have pointed this out in the last 8 years, it has been easy to closet away and to forget.

Yes, if methane outputs (and inputs) on continental slopes accelerated during warming from the latest Paleocene through the early Eocene, and they decelerated during cooling into the middle Eocene, there should be evidence of this in sediment sequences that accumulated in locations of major methane storage and release. More specifically, we should find anomalous accumulations of 13C-depleted carbonate and 34S-enriched barite in lower-middle Eocene sediment deposited along continental slopes (i.e., where

C874

the SMT became fixed for some time). We should find evidence for enhanced methanogenesis in Paleocene-lower Eocene sediment at such locations (i.e., in sediment well below the seafloor at the time). This should include 34S-depleted pyrite and 13C-enriched carbonate. We should find biomarkers for methanotrophy during the PETM and other times of purported aerobic oxidation, as well as chemoherms.

Very few, if any, sequences examined for paleoceanographic interpretations have targeted such locations. There is the paper on 34S-depleted pyrite in early Eocene sediment in the ACEX holes (Ogawa et al., EPSL, 2009); there is an intriguing paper on anomalous 34S-enriched barite in middle Eocene slope sediments across Israel (Bogoch et al., J. Sed. Pet., 1987); there are others. But it is difficult to get excited about these and other works, which have been published generally without considering dynamic seafloor methane systems in the time domain. Basically, as stated in the manuscript, there is ZERO positive evidence for the overall idea of a large and dynamic gas hydrate capacitor in the early Paleogene. I am unsure, however, whether we have a case that very few people have looked for the evidence (and under the umbrella of a geochemical modeling context), or we have a case that the entire idea is wrong. Maybe the current manuscript will spawn some studies . . . if the overarching idea is correct, the evidence must be there.

So, do I thank you or curse you for this comment? In terms of making the paper truly engaging, I suppose I should go “out on a limb” and add a paragraph on this matter.

4/ I have not thought about this interesting idea and I am not sure how to respond other than to say that, already, the speculation is high (especially after seriously thinking about a good response to comment 3).

Will incorporate the minor comments.

Jerry