

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

S. Kasten (Referee)

skasten@awi-bremerhaven.de

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Comments by Sabine Kasten on "Methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events: setting appropriate parameters for discussion" submitted to Climate of the Past by G.R. Dickens.

It was a pleasure to read this contribution and to see this comprehensive compilation of arguments for and against the gas hydrate dissociation hypothesis in order to pave the

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way for a re-evaluation and re-discussion of the role of gas hydrates/methane seepage in the evolution of the PETM and other hyperthermal events. I was particularly happy to see several new aspects introduced into the discussion – in particular the role of anaerobic oxidation of methane (AOM) as well as the associated formation of iron sulfides and its possible feedback on the global sulfur cycle.

This manuscript makes a very valuable contribution to CP and I am convinced that it will stimulate new discussion and further research – concerning geochemical conditions and biogeochemical processes that occurred during and across the PETM in particular and in association with AOM above gas hydrate systems in general. I definitely recommend publication of this contribution in CP, however, some minor revision is required to correct and specify some of the statements related to the geochemical/diagenetic processes.

The major points are listed below. I have also added some ideas/further points from the side of non-stady state diagenesis which might perhaps also be worth being considered with respect to the “PETM discussion”.

1) On page 1154, 2nd paragraph there are several statements that are either confusing (at least for me) or not correct.

I do not agree with the statement that the burial of authigenic carbonates removes the “ ^{13}C -enriched” HCO_3 . It is rather the opposite case, i.e. authigenic carbonates form in relation with the anaerobic oxidation of methane. AOM leads to the formation of ^{13}C -depleted DIC (which consists mostly of bicarbonate) and this increases alkalinity and produces oversaturation and subsequent precipitation of authigenic carbonates. These authigenic carbonates (formed from light methane-derived carbon) are distinctly ^{13}C -depleted and show typical $\delta^{13}\text{C}$ values between -40 and -60 permille.

Page 1154, line 20 and page 1158, ls. 8/9: To my knowledge bicarbonate is NOT produced during/by methanogenesis but consumed due to CO_2 reduction. It is – in contrast - the anaerobic oxidation of methane which produces bicarbonate and leads

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to oversaturation of carbonates (see above!).

As has also been modeled and presented by Luff and Wallmann (2003), during periods of active methane/fluid seepage a significant fraction of bicarbonate produced by AOM is not removed from the pore fluids by authigenic carbonate precipitation but can escape into the bottom water. It is important to note that considerable amounts of isotopically light C (methane as well as bicarbonate) only seem to escape across the sediment/water interface during episodes/times of active fluid seepage/venting. During a fluid migration event high amounts of free methane gas which had previously accumulated up to critical pore pressures below the GHSZ are assumed to migrate up along preferential pathways into shallower sediment and across the sediment/water interface. This fluid migration event causes the formation of the “gas hydrate capacitors” at shallow sediment depth. After the fluid migration event the sediment system above the uppermost gas hydrate layer/s has been shown to be mostly diffusion-controlled and gas hydrates slowly dissolve due to methane undersaturation of the pore fluids produced by AOM (e.g., Lapham et al. 2010; Nöthen and Kasten, in press). Measured alkalinity profiles at many of such “dormant” or relatively inactive cold vent sites overlying gas hydrates demonstrate that there is not a significant gradient thus flux of alkalinity/bicarbonate into the overlying bottom water.

2) Page 1160, 1st paragraph, last sentence: The statement/wording in this sentence is a bit misleading. “CH₄ output” here suggests that you mean escape of CH₄ from the sediment into the water column. However, I assume that you refer to the escape of methane from the gas hydrate bearing layers into the overlying sulfate/methane transition zone because iron sulfides do certainly NOT form when methane escapes from the sediments but - in contrast - when methane is consumed i.e. oxidized anaerobically within the sediments overlying gas hydrates.

Thus the presence of massive enrichments of iron sulfides suggests that high amounts of methane have been consumed in the seabed - otherwise the high amounts of H₂S required for the formation of the iron sulfides would not have been available. Thus I

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am convinced - and also several studies have shown this as well - that AOM occurring above gas hydrate layers consumes large amounts of sulfate/sulfide (e.g. Kasten et al. 1998; Hensen et al. 2003; Riedinger et al. 2005; Jørgensen et al. 2004). However, large amounts of iron sulfides in a particular layer can only form if the sulfate/methane transition zone remains fixed at a particular sediment layer for a prolonged period of time and if the transport processes in the pore space of the sediment are controlled by diffusion. Thus large enrichments of iron sulfides form during times of “non-venting”. The efficiency of the trapping of hydrogen sulfide produced by AOM is dependent on the amount and reactivity of iron oxides available. In high-accumulation systems like off large river systems or along many continental margins and slopes (perhaps like also found in the Arctic) the amounts of reactive iron oxides are so high that any sulfide produced by AOM is trapped in the sediment as iron sulfides.

3) It is well known that profound changes in environmental/geochemical and oceanographic conditions – as those documented for the PETM - lead to distinct nonsteady-state/transient diagenetic phenomena – like migrating or fixed redox boundaries and biogeochemical reaction fronts (see above!). This should definitely be considered when interpreting geochemical signals across the PETM.

Furthermore, several studies have demonstrated that in sediments overlying methane- or gas hydrate-charged sediments, AOM often occurs at several to several tens of meters sediment depth. Thus “active” diagenetic overprint or formation of authigenic minerals or dissolution of primarily deposited minerals typically occurs in deep seafloor sediments – several tens of thousands of years after their deposition. In other words the age of the authigenic mineral or the time of its formation is significantly younger than the age of the sediment layer that hosts this mineral precipitate. So the age of some of the geochemical signatures across the PETM (^{13}C signatures of carbonates and massive occurrence of iron sulfides) may not correspond to the age of the surrounding sediment but may be much younger. So, to formulate a provocative question: What if the observed overprint/geochemical signatures did not form at the onset or dur-

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ing the PETM but rather much later when the system returned to a new steady-state – and the redox boundaries and reaction fronts (like the sulfate/methane transition zone) were fixed for a prolonged period of time above the “remaining” gas hydrate capacitor – coinciding with an age of ~ 56-50 Ma. The return to a pre-PETM condition was possible because warming of bottom waters and heat propagation into the sediment ceased/stopped and no further high pore pressure due to formation of free gas below the base of the GHSZ and thus venting occurred.

4) When reading the discussion about the likely mechanisms/sources that have caused a series of ^{13}C -depleted carbon inputs into the ocean I thought that it might have been produced by the continuous shoaling of the base of the GHSZ due to the observed warming of bottom waters during the PETM – which might however have triggered a discontinuous release of methane. Perhaps ^{13}C -depleted carbon input occurred repeatedly because free gas that must have successively formed below the GHSZ needed time to grow to amounts producing sufficient pore pressure to induce an upward methane migration event. After such a fluid migration event it took some time to “recharge” the amount of free gas below the base of the GHSZ due to continuous warming and dissociation of the hydrates from below in order to produce the next venting event due to critical pore pressure.

Minor comments and corrections

Page 1151, line 28: it has to be “Müller”

Page 1154, l. 28: ... greater amount “of” carbonate dissolution ...

Page 1160, l. 1; page 1170, l. 21: it has to be “Schulz”

Page 1167, l. 26: deposition

Page 1170, l. 19: anaerobic

Page 1172, l. 10: it has to be “Röhl”

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