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Discussions

Interactive comment on “Methane hydrate stability and anthropogenic climate change” *by* D. Archer

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General Comments: I comment on this manuscript as a paleoceanographer, and do not have the qualifications to comment knowledgeably on aspects related to modeling and modern day hydrate occurrence. What I liked in this manuscript (as I did the first time I reviewed it) is that it offers a review of the question of methane hydrate stability and the possibility of climate dissociation and its effects on future climate, with the author deciding that gas hydrate destabilization as the result of anthropogenic global warming is not very probable in the near future. This field of research is complex and interdisciplinary, as well as rapidly expanding, so that an overview with many references to the general literature is very welcome. When I read this after its earlier submission, it was the very first paper that I had seen that combined so much information on the topic from so many different sources. As a result of the rapid expansion of knowledge of gas hydrates, however, it seems to me that that the manuscript is by now somewhat out of

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date, as it appears to not have been updated since I last reviewed it. It seems to me that the paper, maybe because of its wide scope, lacks depth in several aspects. Since my expertise is mainly in paleoceanography, I would say specifically that the paleo-debate is somewhat shallow, but maybe this is how much in detail the manuscript should go and still maintain interest in a broad audience. In addition, I think that the manuscript still (after earlier reviews) is somewhat rough around the edges, with typos and such persisting from its earlier version. I would recommend publication with somewhere in between minor and major revision; nothing major as to organization and overall layout, but a bit more than minor as to correcting typos and providing updated references.

A general point of discussion/update of manuscript: This manuscript clearly points out various problems with the 'gas hydrate hypothesis' for the Paleocene Eocene Thermal maximum which is important for the discussion of possible importance of gas hydrate dissociation in the future (and possible effects on biota). In my opinion this section specifically needs to be updated, not in the least because of publication in Science (314) of a short note by Pagani et al., the author of this manuscript being one of the 'et al'. This argument includes the following components: 1. we do not know the extent of the carbon isotope excursion at that time precisely (around 2.5 permille? around 5 permille?), and we do not know the CO2 concentration in the atmosphere (nor the size of the oceanic reservoir) at the time just before the warming event. 2. therefore we can not easily figure out what process of emission of isotopically light carbon was responsible. 3. IF the lower value of the isotope excursion is correct, AND IF the source were gas hydrates (with a carbon isotopic signature around -60 permille), AND IF the atmospheric CO2 levels before the event were indeed around 1000-1500 ppm rather than around 500 ppm as assumed earlier (˜1995), THEN it appears that we see larger effects on dissolution in the oceans and on global temperature increase than warranted by the amount of carbon emission needed to explain the excursion.

In my personal opinion the author present an excellent set of points, but I think that the problem also may lie in a lack of our understanding of the carbon cycle (as also stated by trhe author at various places - i just would like to see it a bit more emphasized). After all, as the author mentions (but does not stress), the GLOBAL effects of dissolution are not at all well defined (eg. Colosimo et al. 2005: little effect on CCD in Pacific), although dissolution was severe in the Atlantic (and reached to much shallower depths than shown in Zachos et al. 2005, see eg Thomas 1998 for compilation). We thus do not really know the limits imposed by the dissolution as observed. In addition, I recently heard a presentation by G. Roe (University of Washington) who argued that the climate sensitivity (degrees of globally averaged warming per doubling of CO2) may very well depend upon the basic climate state, i.e., sensitivity in the late Paleocene could have been larger (6-8 degree per CO2 doubling) than it is today (IF estimates 1,5-4.5 degree in IPCC are correct). IF Roe's argument is correct, the argument from climate sensitivity would become invalid.

I think we may need to think about more possible far-out hypotheses. The ODP Leg 302 data show that the Arctic was (at the time of the PETM) brackish and stratified - the manuscript needs to be updated on temperature estaimtes for shallow water Arctic). IF we need more carbon input than we get by assuming that we know the extent of the CIE, as given by the oceanic record (˜2.5 - 3.0 per mille), and assuming that the source of carbon was methane from gas hydrates (isotopic composition ˜ -60 per mille) -as argued here, as well as in Pagani et al. 2006 than we could think of the Arctic as a (temporary) reservoir of either/both CO2 and CH4, collecting, then releasing what volcanic carbon compounds - similar to smaller scale processes in lakes such as Nyos and Kivu. We need a fast process to release light carbon into the environment, with the timing of release a maximum a few thousand years. IF it is true that there were more hyperthermal events (events like the PETM, but less extreme), then we need a process that could be triggered by Milankovich-type changes in climate (temperature, precipitation), and a process which could happen more than once (Lourens et al., 2005), thus we need a reservoir that can be recharged on timescales of about 1 million years or less. We need an explanation why hyperthermals occurred in the late Paleocene - early Eocene interval only, if we believe Thomas and Zachos, 2000; Thomas et al., 2000. We could (wildly) speculate that the Arctic Ocean behaved like a much larger version of the stratified Lake Kivu in the African Rift valley, in which there are stored large amounts of volcanic CO2 as well as methane from bacterial action (partially on organic matter, partially on the CO2; Schoell et al., 1988; http://perso.wanadoo.fr/mhalb/kivu/eg/eg_1d_densite.htm. Volcanic CO2 in the Arctic could have been derived from the North Atlantic Volcanic Province, and/or from kimberlitic volcanism in Canada (late Paleocene - early Eocene ages; Creaser, R. A., Gruetter, H., Carlson, J., and Crawford, B., 2002, Macrocrystal phlogopite Rb-Sr dates for the Ekati property kimberlites, Slave Province, Canada: evidence for multiple intrusive episodes in the Paleocene and Eocene: Lithos, v. 76, p. 399-414. One could imagine that the Arctic stratification was broken up as the result of changes in salinity (evaporation, precipitation), leading to large emission of greenhouse gases. Quick notes: lake Kivu has a temperature of 20-25oC, an area ˜ 2400 km2; a volume ˜ 560 km3; depth ˜ 500m. The lake is stably stratified, and contains huge amount of CO2 (˜ 250-255 km3 CO2 if recalculated to STP) as well as methane (55-65 km3 CH4 at STP); even so, the lake is way under saturation. The methane is said to be bacterial (fermentation and CO2 reduction), with d13C = -56 o/oo; the CO2 volcanic (d13C -2 to -5 per mille) (Schoell et al., 1988). Using Arctic as mega lake Kivu storage ended with greater connection of Arctic to world oceans, ending of volcanism in North Atlantic (sinking of ridges). Was there enough arctic ocean at the time? We assume that the Eurasian Basin did not yet exist (opened in Chron 24), but the Amerasian Basin is probably much older (Early Cretaceous, Lawver et al. 2002), and that basin was similar in size to the present Amerasian basin (surface area ˜ 3 million km2. We do not know its depth; data on benthic forams in delta in MacKenzie - Beaufort Basin indicate that there was a deep basin to the north, probably at least 1000 m deep, probably much deeper - present basin is 3700-4000 m deep and there's thick piles of turbidites on its bottom. Back of envelope scribbles show that such a volume could hold at least 200*10ˆ6 km3 gases at STP.

Obviously, this is just a wild speculation - I only want to argue that we just may not have looked at enough possible processes within the carbon cycle to understand past events, and some sentences refelcting this uncertainty might be nice. The author should update the section on possible multiple events- there is now much more evidence (more publications) on the mid paleocene event, the Elmo event (about 2 million after PETM) and the X event (about 1 my after Elmo), and maybe the Ypresian/Lutetian event at 49Ma. These events have been argued to be linked to carbon isotope anomalies, and if Fehn et al were correct in estimates of age of gas hydrate deposits such events could not be so closely spaced in time, probably.

Specific Questions/Remarks/Comments:

994: Line 20: As much? 995: Line 14: by far the greatest portion of which methane?? In the atmosphere clearly must have been generated by life, since residence time is 10 years. You mean ‘present in the atmosphere at any one time? 996, line 4: methanogenesis, not mathanogenesis Line 6: ‘These pathways’ probably means pathways in ‘fresh water’ and ‘salt water’ environments, but this is not very clear from the text. Lines 21-22: I do not quite understand the reference to Blake Nose; as far as I know, at eg Site 994 there is the same relation as described for ‘at other locations’, i.e. ‘they diffuse toward their mutual annihilation’ - see e.g., fig 4 in Dickens et al 2003, with no sulfate below ˜20 m or so? Is observation only for site 997 (which I think - see Borowski 2004, Chem. Geol.) Line 22: typo in use of period, comma after ‘depleted’. 997. line 12: ‘small organic compounds’ - low molecular weight would sound better. 998, line 12: something wrong in this sentence - ‘(order 10%..’? what is meant? ‘on the order of 10%? Lines 21-22: ‘Ozone photolyzes .. to yield OH’ ; I think ‘photolysis’ is the same as ‘photodissociation’, which is the break down of a chemical compound by light energy. So that means that that ozone can not produce OH by photolysis - it’s got to get that H somewhere by a reaction other than breakdown of its molecule (same for NO2). 999, line 19: the record in ice cores, and its ‘smoothing’: would have been good to specifically mention these time scales; if I remember correctly Thorpe et al. mentioned that at that time ice cores had not been sampled at higher resolution than 50 years (not quite ‘smoothing’); they did mention that higher resolution work was possible. 1000, line 2: the verb ‘finds’ appears not really ideal here. 1001, line 5; in the UPPER few cm (insert ‘upper’); line 21: att he base of the hydrate and gas zone: what depth below sea floor? 1002, line 12-13: ‘methane released to the dissolved phase’ - this sentence is not clear to me. What exactly is ‘the dissolved phase’? sea water or pore water? Line 20: I would say ‘sediment on active margins’ rather than ‘sediments in active margins’; more quickly than ‘those on’; insert ‘those on’. 1003, line 6 and on: definition of ‘mud volcano’ is rather incomplete, needs some information on scale, whether always linked to methane hydrates or not; needs more references (who says that are 1800 mud volcanoes around the world?). What is the difference between a mud volcano and a large pockmark (1007, section 2.4.2)? topics need to be defined more (since paper addresses a wide audience). There is a return to mud volcanoes (and pockmarks) on 1016, lines 1-8; there also definitions are not very clear. Lines 13 and on - bubbles and such (also 1009, lines 2-4): There are various papers by Zhang on bubbles and gas hydrates, as quoted in e.g., Zhang, Y., and Kling, G. W., 2005. Dynamics of lake eruptions and possible ocean eruptions. Ann. Rev. Earth Planet. Sci. 34, 293-324. Some of these papers are in my opinion relevant to this discussion, which appears a bit incomplete. 1006, lines 1920: how about reference to various papers by Levitus et al (2005, Geophys,. Res. Lett.) documenting that present intermediate waters in the oceans are warming as a response to present anthropogenic global warming? 1008, line 21: it would be better to say ‘lowering of sea level’ rather than ‘sea level change’; I do not see that rising sea level could lead to has hydrate dissociation. If so, please discuss. 1010, line 17: what determines this lifetime: any temperature influence? 1012, line 15-on: in my opinion it would have been good to mention that this distribution of sediment with organic carbon $>$0.5% or $>$1% (15-30% of sea floor 500-3000 m) is typical for the PRESENT oceans (thus not necessarily for oceans of the past). In my opinion there is evidence from the fossil record of deep-sea faunas (Thomas, 2007; see http://ethomas.web.wesleyan.edu/publications.htm) suggest that this may have been considerably different in the past Greenhouse World - with possibly more transport of organic matter to the seafloor in regions which are now oligotrophic gyres. 1014, line 13: I agree that methane oxidation in the oceans could lead to oxygen depletion (thus possible unpleasant results for faunas in the deep sea). Note that we should be able to recognize anoxic events of the past (e.g., laminated sediments). 1015, lines 18-on: it might have been more useful for the reader if there had been a table listing these occurrences (structural deposits). 1016, line 12: permafrost covers 20% of the terrestrial surface of the earth: any estimates of volume (i.e., to what depth?) 1017, line 5: is this just peat in permafrost regions? Not quite clear - seems a bit low ofr all peat on earth 1018, lines 24-25: delete ’within historical times’ - that is impliked in ’in the last centuries’. 1019: hydrates as fossil fuel. This section needs updating - e.g., results of hydrate research in India - see http://energy.usgs.gov/other/gashydrates/india.html. There have been various conferences on commercial use of gas hydrates, with estimates of actual use of gas hydrates over shorter timescales than suggested here. (e.g. http://www.informz.net/hartconf/data/images/hydrates_0906HEP.pdf). Line 15: Nankai (not Nankia) 1021-1022; Storegga slide. In my opinion this text is not clearly written. The arguments for/against hydrate involvement in the causation of the slide are not made clear to me (and I am familiar with the topic). The possible link to the 8.2 ka cold event is not explained well: how does methane emission lead to cold events? Or did the cold event lead to the slump because of sea level fall (if ice caps grew)? 1023: Implications. It might have been interesting to refer at least to some other possible hydrate-linked submarine slides (e.g., Maslin et al 2004), e.g. in Mediterranean, on Amazon fan and list timing as related to glaciation/deglaciation events. 1023, line 13-14: I suggest ‘ might be cause for concern’ rather than ‘might be ..concerning’. Line 18: duration PETM in latest estimates 170 kyr (Westerhold et al., in press in Paleoceanography; Roehl et al 2006 in Bilbao conference volume, may 2006). In earlier literature age estimates ranged from 220 kyr (Röhl, U., Bralower, T.J., Norris, G. & Wefer, G. 2000. A new chronology for the late Paleocene thermal maximum and its environmental implications. Geology, 28: 927-930) to ˜ 120 kyr (Farley, K.A. & Eltgroth, S.F. 2003. An alternative age model for the Paleocene-Eocene thermal maximum using extraterrestrial 3He. Earth and Planetary Science Letters, 208: 135-148). Kennett & Stott 1991 did not give a timescale of 140 kyr. Line 25: note that the other carbon isotope anomalies also occurred during periods of peak warming. 1024, line5: note that there are also non-oxygen isotope records of temperature, using different and independent proxies, thus reinforcing the hypothesis that there WAS indeed global warming and we are not looking at some problem in the oxygen isotope records (Mg/Ca, Tex 86). Zachos, J.C., Wara, M.W., Bohaty, S., Delaney, M.L., Petrizzo, M.R., Brill, A., Bralower, T.J. & Premoli Silva, I. 2003. A transient rise in tropical sea surface temperature during the Paleocene-Eocene thermal maximum. Science, 302: 1151-1154.; Zachos, J.C., Schouten, S., Bohaty, S., Quattlebaum, T., Sluijs, A., Brinkhuis, H., Gibbs, S. & Bralower, T.J. 2006. Extreme warming of mid-latitude coastal ocean during the Paleocene-Eocene Thermal Maximum: Inferences from TEX86 and Isotope Data. Geology, 34(9): 737-740; Sluijs, A., Schouten, S., Pagani, M., Woltering, M., Brinkhuis, H., Sinninghe Damsté, J.S., Dickens, G.R., Huber, M., Reichart, G.-J., Stein, R., Matthiessen, J., Lourens, L.J., Pedentchouk, N., Backman, J., Moran, K. & the Expedition, S. 2006. Subtropical Arctic Ocean temperatures during the Palaeocene/Eocene thermal maximum. Nature, 441(7093): 610-613. Tripati, A.K. & Elderfield, H. 2004. Abrupt hydrographic changes in the equatorial Pacific and subtropical Atlantic from foraminiferal Mg/Ca indicate greenhouse origin for the thermal maximum at the Paleocene-Eocene Boundary. Geochemistry, Geophysics, Geosystems, 5(2): doi:10.1029/2003GC000631. Line 13: carbon isotopes (plural) rather than carbon isotope. Line 20: I do not understand ‘the resulting necessity to use multiple species’; the problem with the dissolution is that there is NO carbonate, so no proxies using carbonate can be used, and we can not get a carbon isotope signal (unless there is organic matter present). Line 26: I would say that presently the consensus is moving towards much higher atmospheric pCO2 levels before (and after) the PETM - see e.g., Pagani, M., Zachos, J.C., Freeman, K.H., Tipple, B., and Bohaty, S., 2005: Marked decline in atmospheric carbon dioxide concentrations during the Paleogene. Science, 309, 600-603; see also Pagani, M., Pedentchouk, N., Huber, M., Sluijs, A., Schouten, S., Brinkhuis, H., Sinninghe Damsté,

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J.S., Dickens, G.R. & Expedition-Scientists 2006. Arctic hydrology during global warming at the Palaeocene-Eocene thermal maximum. Nature, 442(7103): 671-675; Pagani et al. 2006 (with Archer as co-author), Science 314. The figure in that mansucript may look better than fig 8 in this manuscript - maybe replace. 1025, line 11: why $<$1000 GtC in warm ocean? This means assuming same distribution of Corg rich sediments as in present oceans at higher temperature? Or what other assumptions made? Lines 13-15: see Sluijs et al 2006 (above) for temperature estimates of the Arctic and confirmation that the Arctic was anoxic (note that these data are for shallow Arctic). Line 20; note that only site where time difference in planktic and benthic records was seen (690) is NOT in the tropics but close to the Antarctic. 1026, lines 15-17: see Eldholm & Thomas for timing of PETM and North Atlantic Volcanic Province; also Schmitz et al 2004). Note that total duration for the volcanic province was several millions of years, but single flows of course much less time. And if we could use the Arctic a some kind of intermediate storage for carbon-gases (CO2, CH4) we might (speculating wildly) make a case for sudden release of large amounts of gas (see above). Lino 20: see also recent paper on volcanoes as triggering PETM-Science 27 April 2007: 587-589. Line 21: there really is NO solid evidence that acidification caused extinction of calcifying organisms - but see also Stoll et al in recent EPSL on update on calcification of nannoplankton. Planktonic foraminifera and calcareous nannoplankton did NOT show a major extinction as has been known for many years - hence the difficulty in defining the Paleocene/Eocene boundary, but only turnover and rapid evolution. Benthic foraminifera: in my opinion hard to argue that extinction was caused by acidification - that acidification was not global (as argued in this manuscript), agglutinated benthic foraminifera also suffered extinction, and shallow water benthic foraminifera suffered less extinction than deep-water forms (see Thomas 2007 for discussion). 1028 line 28: please add some numbers to 'higher initial CO23' - see earlier comments. Add arguments why climate sensitivity would have been less (line 17) - see comment earlier on. 1029: 'clathrate gun hypothesis'. Note also arguments against this hypothesis (and evaluating hydrates vs wetlands) in Maslin, M. A., and Thomas, E., 2003. Balancing the deglacial global carbon budget: the hydrate factor. Quaternary Science Reviews, 22: 1729-1736; doi: 10.1016/S0277-3791(03)00135-5. In general, Kennett did not consider the carbon isotope records available, a major problem for his hypothesis. 1033, line 19: those IN coastal areas? (add ’in’) 1033-1034: it would be good to insert some quantitative information rather than say ’century timescale response’ and ’geological timescale response’ - this leaves something of a problems with processes on several centuries to millennia. Such timescales are too long for ’century scale’ , but may be too short to resolve in the geological record (except at unusual locations).

Interactive comment on Biogeosciences Discuss., 4, 993, 2007.